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Lectures on chemistry and explosives

Charles Edward Munroe, United States Naval Torpedo Station (Newport, R.I.), United States, United States. ...

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LECTURES

ON

CHEMISTRY AND EXPLOSIVES,

DELIVERED TO THE

SUMMER CLASS OF OFFICERS OF 1888,

AT THE

TORPEDO STATION,

THE MILITARY SERVICE INSTITUTION
PRESENTED BY
OF THE U.S.

BY

PROF. CHARLES E. MUNROE, S. B., F. C. S. &c.,

CHEMIST TO TORPEDO CORPS.

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LECTURE I.

CHEMISTRY.

When treating of the subject of explosives and pointing out the applicability of these substances to certain desired uses, it is quite important that considerable attention should be given to their composition, methods of production and chemical and physical properties, but this cannot be done with precision and without circumlocution, except by the use of the formulas and language of chemistry. As, however, chemical nomenclature and the meaning of many of the terms employed in chemistry have undergone many changes in recent years, and, as your professional duties have necessarily prevented you from keeping informed regarding these changes, it seems wise, in order that it may be perfectly understood what meaning is to be attached to the conventions used, that we should devote a portion of the limited time at our disposal to a hasty review of this science, illustrating it so far as circumstances permit by appropriate experiments.

Chemistry is a material science and deals with the properties of the matter of which substances are composed. So does Physics also, hence at the outset we must distinguish between the provinces of these two closely related sciences. For this purpose let us take a mass of sugar. On inspection we find it to consist of small crystals, having a vitreous luster and, in the mass,

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a white color. But what is most noticeable is that we find, on trial, that the sugar possesses a marked sweet taste. In fact, we know from our daily experiences that this sweet taste is a characteristic and inherent property of the sugar. Let us now grind this sugar in a mortar and the result is that we eventually reduce it to so fine a powder that the crystals disappear from view to the naked eye, the luster becomes dimmed, and the color becomes uniformly white, yet, on trial we find it to still possess its characteristic sweet taste. Let us now treat it with water and soon the mass disappears wholly from view owing to its being dissolved by the water, yet on testing the solution we detect the presence of the sugar by its characteristic sweet taste.

Let us now take another mass of sugar, place it in a platinum dish and heat it over a lamp. We first observe that the mass fuses, but if we test the mass at this stage we still obtain the characteristic sweet taste. We continue the heating and we next observe that the mass begins to blacken and to yield dense fumes, and that this continues until the mass in the dish attains the appearance of charcoal. On testing this mass we find that the characteristic sweet taste has wholly disappeared, and that in place of the soluble, white, sweet, crystalline mass, having a vitreous luster, with which we started, we have obtained an insoluble, black, tasteless mass having a sooty luster. Evidently we have obtained by this process a substance or substances wholly unlike sugar, and in the process we have destroyed the identity of the sugar, while by the three preceding processes, pulverization, solution and fusion, we have simply subdivided the mass of the sugar but have not destroyed its identity. A process such as has been exhibited, by which the identity of a substance is destroyed is called a *chemical* process, and

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the change a *chemical* change. The three processes of pulverization, solution and fusion are examples of physical processes and the subdivision, which resulted, is an example of a physical change.

By the application of the physical processes of subdivision, which we have employed in this experiment, we have discovered that we can separate *masses* of matter into very small portions which still possess the characteristic properties of the *mass*. These smaller portions of matter in which the characteristic properties of the substance inheres are called *molecules*. By the application of the chemical process we are able to subdivide the molecules into their constituent portions of matter. These smallest portions into which the molecules can be subdivided are called *atoms*. Looking back we find that *atoms* combine to form *molecules*, and *molecules* cohere to form *masses*.

It is by means of chemical processes that the chemical properties of substances may be studied, and the constitution of the many bodies which exist in nature and in art determined. There are several of these processes, the first one which we have employed in the decomposition of the sugar being known as the process of Analysis.

As an example of the second let us take three grams of sulphur and eight grams of copper, both in a finely divided condition, and mix them well together in a mortar. Then place them in an ignition tube of glass and heat them in a flame. Now no matter how long we rub them together in the mortar we still can distinguish each substance by its characteristic color, luster and other properties, and so too on heating, although the sulphur fuses, the two substances remain quite distinct, until suddenly we observe incandesence to begin and extend throughout the tube, and we then find the substance in

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the tube to be homogeneous throughout and to possess properties which are unlike either the copper or the sulphur from which it is formed.

Again, let us place a quantity of finely divided iron in a thin crucible and weigh the whole. Then heat the crucible and contents over a lamp. Soon we observe a glow about the edges of the mass of iron which extends throughout the whole even after the source of heat is removed, and on allowing the crucible and contents to cool and weighing it again we find it has very decidedly increased in weight.

It is evident in both these experiments that a union has taken place; that there has been a building up process going on. A process such as this is known as Synthesis.

Next, let us take a solution of common salt and add to it a solution of nitrate of silver. On so doing we at once observe the formation of a dense, curdy, white precipitate which a chemist knows is due to the formation of silver chloride. This is produced by the interchange of atoms between the molecules of the compound substances, common salt and nitrate of silver. A process of interchange such as this is known as Metathesis.

Next, let us take some hydrochloric acid and plunge in it a piece of metallic zinc. We at once observe that bubbles of gas are given off and, if we continue the process long enough, that the zinc entirely disappears. By evaporation we can obtain the zinc in a solid state again, but it will be in combination with chlorine as zinc chloride. This has been brought about by the replacement of the hydrogen, which was united with the chlorine, by the zinc.

Again, let us take a solution of copper sulphate and place in it a bright strip of iron. If we remove the iron

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after a few moments we shall find it to be well coated with copper. Here we have the iron replacing the copper in the compound molecule. Such a process as is shown by these last two experiments is called Replacement.

Sometimes two or more of these processes may take place almost simultaneously, as, for instance, in this experiment when we pour concentrated nitric acid upon metallic tin with the production of a white powder and dense red fumes. Here we have both the processes of analysis and synthesis going on together.

By testing all bodies by the the process of analysis we find that they may be divided into two distinct chemical classes:

1st. Those bodies which cannot by any means at our command be analyzed or subdivided into other substances.

2nd. Those bodies which can be analyzed.

Those bodies which belong to the first class are called Elementary substances, and those bodies which belong to the second class are called Compound substances. The number of elementary substances is, of course, not accurately known, but there are about seventy substances which are now placed in this class. The number of compound substances is so great as to be almost immeasurable.

Of course we can prepare substances by mixing together portions of different elementary substances, or of different compound substances, or of different elementary and compound substances just as we did with the copper and sulphur, or the sugar and water, but, as has been pointed out, these are simply Physical Mixtures.

It will at once be seen that, when stating the percentage composition of chemical substances as the result of our analysis, we give the proportions by weight in which

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the elementary substances or radicles exist in the molecules, and, as chemical substances are homogeneous, this proportion holds true for any mass of the substance. In stating the results of the analysis of a mixture, the results only show the proportions of the various chemical substances which are found existing in that small portion of the mass which we have actually examined, and they will not hold precisely, though they may approximately, for the whole mass, since such a mass can only approximate to perfect homogeneity.

On examining by physical and chemical means the various chemical substances with which we meet, we find marked differences to exist between them, each possessing certain characteristics which are inherent in its molecules. By analysis we find that these differences may be due either

(1) To a difference in the kind of atoms in the molecule.

(2) To a difference in the number of atoms in the molecule.

(3) To a difference in the arrangement of the atoms in the molecule.

We have in common salt and saltpetre an example of the first kind of difference. Here the molecule of common salt contains atoms of sodium and chlorine, while the molecules of the saltpetre contain atoms of potassium, nitrogen and oxygen.

We have in corrosive sublimate and calomel an example of the second kind of difference. The molecules of both of these substances are composed of atoms of mercury and chlorine, but while the molecule of corrosive sublimate contains but one atom of mercury and two atoms of chlorine, the molecule of calomel contains two atoms of mercury and two atoms of chlorine.

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The difference in behavior of these substances is shown when we produce them as we do in this experiment, by the calomel at once precipitating out as a voluminous white precipitate, while the corrosive sublimate remains in solution.

We have in starch and cotton an example, among commonly known substances, of the third kind of difference. The molecules of both of these substances have been found to contain the same number of the same kinds of atoms, viz., carbon, hydrogen and oxygen. Here the difference then can only be due to a difference in the arrangement of the atoms in the molecule.

This difference is better illustrated by the molecules of acetic acid and methyl formate.

From the consideration of the foregoing results we arrive at the following definition of Chemistry.

Chemistry is that branch of physical science which treats of the atomic composition of bodies, and of those changes in matter which result from an alteration in the kind, the number, or in the relative position of the atoms which compose the molecule.

It is evident that as chemical substances are composed of matter they must have weight, and that this will be true also of their constituent atoms. Attempts have been made to determine this weight, but owing to the extreme smallness of these atoms we have only been able to ascertain their weights approximately in terms of the ordinary standards of weight. By taking, however, the weight of a given volume of the lightest known substance, hydrogen, as a standard, we have been able to ascertain with precision the relative weight of the other substances. The volume of hydrogen, which is taken as a standard, is the smallest volume which is ever known to exist in a compound molecule. The proportional

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numbers which are thus obtained are called the Atomic weights.

Thus calling the weight of the atom of hydrogen unity, or 1, we have for the atom of oxygen 16, nitrogen 14, chlorine 35.5, carbon 12, and so on for all the elements known, meaning in every case that the atom of the ele. ment mentioned is that number of times heavier than the atom of hydrogen.

In placing these names upon the blackboard I have written them at length, but it becomes evident that, as they are to be used very frequently in chemistry, it will be very convenient to indicate the substances by some simpler means. It is for this reason that a system of chemical symbols has been devised. A list of the better known elements, together with their symbols and atomic weights, are given in this table:

Name.	Symbol.	Atomic Weight.*	Name.	Symbol.	Atomic Weight.*
Alumininum	Al	27	Molybdenum	Mo	96
Antimony	Sb	120	Nickel	Ni	58.6
Arsenic	As	75	Niobium	Nb	94
Barium	Ba	137	Nitrogen	N	14
Beryllium	Be	9	Osmium	Os	193
Bismuth	Bi	208	Oxygen	O	16
Boron	B	11	Palladium	Pd	106
Bromine	Br	80	Phosphorous	P	31
Cadmium	Cd	112	Platinum	Pt	194
Caesium	Cs	133	Potassium	K	39
Calcium	Ca	40	Rhodium	Rh	104
Carbon	C	12	Rubidium	Rb	85.4
Cerium	Ce	140	Ruthenium	Ru	104.6
Chlorine	Cl	35.5	Scandium	Sc	44
Chromium	Cr	52.2	Selenion	Se	79
Cobalt	Co	59	Silicon	Si	28

*In round numbers.

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Name.	Symbol.	Atomic Weight.*	Name.	Symbol.	Atomic Weight.*
Copper	Cu	63.2	Silver	Ag	108
Didymium	Di	144	Sodium	Na	23
Erbium	Er	166	Strontium	Sr	87
Fluorine	F	19	Sulphur	S	32
Gallium	Ga	69.9	Tantalum	Ta	182
Germanium	Ge	72.2	Tellurium	Te	125
Gold	Au	197	Terbium	Tr	148
Hydrogen	H	1	Thallium	Tl	204
Indium	In	113.4	Thorium	Th	232
Iodine	I	127	Tin	Sn	118
Iridium	Ir	192.6	Titanium	Ti	48
Iron	Fe	56	Tungsten	W	184
Lanthanum	La	139	Uranium	U	240
Lead	Pb	207	Vanadium	V	51.2
Lithium	Li	7	Yttrium	Y	89
Magnesium	Mg	24	Ytterbium	Yb	173
Manganese	Mn	55	Zinc	Zn	65
Mercury	Hg	200	Zirconium	Zr	90

*In round numbers.

Inspection of the table shows that for many of the elements, such for example as hydrogen, oxygen, nitrogen carbon and the like, the first letters of the name, for example H, O, N and C, are used as the symbols. When, however, there are several elements whose names possess the same initial letter, then to distinguish between them we join to the initial letter a second characteristic letter from the name, and thus we get for chlorine Cl, chromium Cr, cobalt Co, Cerium Ce, calcium Ca. Inspection of the table, however, shows that there are several symbols which do not appear to have been derived in either of these ways. Thus we have for antimony Sb, gold Au, iron Fe, lead Pb, mercury Hg, potassium K, silver Ag, sodium Na, tin Sn. Nevertheless, these symbols have

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been derived as those above have, but the Latin names have been used for these last named elements, while English names have been used for the others.

When these symbols are used they signify something more than that the elementary substance they represent is present, for each symbol represents a definite portion, *one atom*, of the elementary substance, and it represents also a definite weight, *the weight of one atom*, of that substance, referred to the weight of the atom of hydrogen as a standard.

By combining the symbols of the elements together we can obtain formulas which represent the composition of the molecules. Thus combining Na and Cl as follows, NaCl, we obtain the formula for common salt, these molecules being made up of one atom of sodium and one atom of chlorine each. The symbols in this formula still represent parts by weight, and thus the formula expresses the fact that a molecule of common salt contains 23 parts, by weight, of sodium and 35.5 parts, by weight, of chlorine.

From this example we learn how to obtain the Molecular Weight of a substance when we know its formula. We have simply to add together the weights of the constituent atoms. Thus the molecular weight of common salt is $23 + 35.5 = 58.5$.

We have found that a molecule may contain a number of the same kind of atoms. To indicate this fact we place a numeral below the symbol of the element. Thus we have the chlorides of mercury, corrosive sublimate $HgCl_2$, and calomel Hg_2Cl_2. The molecule of the first contains one atom of Hg, or 200 parts by weight, and two atoms of Cl, or $2 \times 35.5 = 71$ parts by weight, and its molecular weight is $200 + 71 = 271$. The molecule of the second contains one atom of Hg, or

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$200 \times 2 = 400$ parts by weight, and two atoms of Cl, or 71 parts by weight, and its molecular weight is 471.

By the use of numerals we can also indicate that a number of groups of atoms exist within a molecule. Thus in forming our chlorides of mercury we employed two different nitrates of mercury, which are represented by the formulas $Hg(NO_3)_2$ and $Hg_2(NO_3)_2$. The submultiple used affects all the symbols enclosed in the parenthesis so that we see that each of these molecules contains two atoms of N and $3 \times 2 = 6$ atoms of O.

While the submultiple affects only the symbol above it, or only the symbol enclosed in parenthesis above it, a numeral placed before a symbol or formula affects all the symbols in that expression. Thus 2 NaCl indicates two molecules, or 117 parts of common salt. 5 Hg_2Cl_2 represents five molecules, or 2355 parts by weight of calomel.

By combining formulas together by means of plus (+) and equality (=) signs we may form Chemical Equations and thus express the changes taking place in Chemical Reactions.

Thus the experiments with the copper and sulphur gave rise to a reaction which may be represented by the following equation:

$$Cu + S = CuS$$

The experiment with the iron burnt in air by

$$3Fe + 4O = Fe_3O_4.$$

The reaction of the zinc with muriatic acid by

$$Zn + 2HCl = ZnCl_2 + H_2.$$

The reaction of the iron with copper sulphate by

$$Fe + CuSO_4 = FeSO_4 + Cu.$$

The reaction of the tin and nitric acid by

$$Sn + 4HNO_3 = SnO_2 + 4NO_2 + 2H_2O.$$

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The reaction of the hydrochloric acid and mercuric nitrate by

$$2HCl + Hg(NO_3)_2 = HgCl_2 + 2HNO_3.$$

The reaction of the hydrochloric acid and mercurous nitrate by

$$2HCl + Hg_2(NO_3)_2 = Hg_2Cl_2 + 2HNO_3.$$

To write the equation expressing any given chemical reaction it is essential that we should know what substances enter into and issue from the reaction. This can of course only be ascertained by actually subjecting all the materials to chemical tests. Having this knowledge how are we to write the equation? How are we to know what number of parts of the different substances enter as factors? The first consideration that governs us is that in every equation the sum of the weights of the factors equals the sum of the weights of the products, and that the same number of the same kind of atoms will be found in the products as existed in the substances taken.

Hence, we can proceed to write the equations by placing the formulas for the substances taken on the left hand and the formulas of the products on the right hand, connecting them by the proper signs. Then we proceed tentatively to find the numeral coefficients, using the simplest numbers which will satisfy the equation. In many cases this can be readily done by inspection, but in the more complex reactions the speediest way of determining the numerical coefficients is found in the algebraic method of Simultaneous Linear Equations.

To apply this we write the equation as before, placing literal coefficients before each term in the equation. Then beginning at the left hand and proceeding with each separate symbol we obtain a linear equation for each element, which shows the number of times that the

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element appears in the reaction. Solving these equations and reducing to lowest whole numbers we obtain numerical coefficients which we substitute for the literal coefficients in the original chemical equation.

For example we find when we act on tin with nitric acid that the eventual products are SnO_2, NO_2 and H_2O. Write the equation, knowing the formula of nitric acid to be HNO_3, and the symbol of tin to be Sn:

$$a\ Sn + b\ HNO_3 = w\ SnO_2 + x\ NO_2 + y\ H_2O.$$

(1) $a = w$, (2) $b = 2y$, (3) $b = x$, (4) $3b = 2w + 2x + y$.

As b appears with three values let us assume that $b = 1$, then from equation (2) $y = \frac{1}{2}$ and from (3) $x = 1$. Substracting these values in (4) we have $3 = 2w + 2 + \frac{1}{2}$ $\therefore \frac{1}{2} = 2w$ and $w = \frac{1}{4}$. Hence as by (1) $a = w$ $\therefore$ $a = \frac{1}{4}$.

To sum up $a = \frac{1}{4}$ reducing to whole numbers a = 1

$b = 1$	b = 4
$w = \frac{1}{4}$	w = 1
$x = 1$	x = 4
$y = \frac{1}{2}$	y = 2

And substituting we have

$$Sn + 4HNO_3 = SnO_2 + 4NO_2 + H_2O,$$

an equation which satisfies.

When we compare the formulas of a number of compounds of two elements, one of the elements being common to all the compounds, we discover that the elements possess very different powers as regards the number of atoms of the constant with which they can combine.

Thus let us take the groups

HCl	NaCl	Na_2O
H_2O	$CaCl_2$	CaO
H_3N	NCl_3	CO_2
H_4C	CCl_4	SO_3

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One atom of Cl can combine with, as in HCl, or replace, as in NCl_3 and CCl_4, one atom of H. One atom of C can combine with, as in H_4C, or replace, as in CCl_4, four atoms of H, and a similar power exists, though in different degrees, in all the other elements. This property which determines the number of atoms of an element with which another will enter into union is called the Combining Power of the atom, and this combining power is measured in terms of the hydrogen atom. When the element combines with some other element than hydrogen we can measure its combining power, in terms of hydrogen atoms, by comparing it with the element united with it, provided we know the combining power of this last element. Thus taking the first column above, the combining power of Cl must be 1, of O, 2; of N, 3; and of C, 4. Taking the second column we know Cl = 1H, then Na = 1, Ca = 2, N = 3 and C = 4. Taking the third column we have O = 2H, then Na = 1, Ca = 2, C = 4 and S = 6.

The measure of the combining power is called the Valency of the atom, or its Combining Value, in terms of hydrogen atoms.

Our system of notation enables us to indicate the valency of an atom, for we have simply to attach to the symbol either Latin numerals or dashes. Thus,

$\overset{\text{I}}{\text{H}}, \overset{\text{II}}{\text{O}}, \overset{\text{III}}{\text{N}}, \overset{\text{IV}}{\text{C}}, \overset{\text{I}}{\text{Cl}}$., or thus, H-, -O-, -N-, -C-, Cl-.

When the symbols are combined in formulas, the dashes between any two symbols are counted for each symbol. Thus,

$$\text{H–Cl, H–O–H, } \begin{array}{c}\text{H}\\|\\\text{H–N–H,}\end{array} \quad \begin{array}{c}\text{H}\\|\\\text{H–C–H.}\\|\\\text{H}\end{array}$$

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When we compare a group of formulas in which both elements are constant, but the number of atoms is variable, we observe that such formulas can only result through a change in the combining power of the atoms of one or both of the elements. Thus,

VALENCY OF SOME OF THE ELEMENTS.

VALENCY.		I		II		III	I		IV	II		V	III	I		VI	IV	II
	F	H F	O	H_2O	B	BCl_3		C	CH_4	CO	N	N_2O_5	NH_3	N_2O	S	SO_3	SO_2	H_2S
	H		Hg	$HgCl_2$	Au	$AuCl_3$	AuCl	Si	$SiCl_4$		P	PCl_5	PH_3	.	Se	H_2SeO_4	$SeCl_4$	H_2Se
	Li	Li Cl	$[Hg_2]$	$[Hg_2]Cl_2$				Pb	$PbCl_4$	$PbCl_2$	As	AsF_5	AsH_3		Te	TeO_3	$TeCl_4$	H_2Te
	Na	Na Cl	Cu	$CuCl_2$				Sn	$SnCl_4$	$SnCl_2$	Sb	$SbCl_5$	SbH_3		Cr	CrO_3	$[Cr_2]Cl_6$	$CrCl_2$
	K	K Cl	$[Cu_2]$	$[Cu_2]Cl_2$				Zr	$ZrCl_4$		Bi	Bi_2O_5	$BiCl_3$		Mn	MnF_6	MnF_4	MnF_2
	Ag	Ag Cl	Cd	$CdCl_2$				Al	$[Al_2]Cl_6$		Cl	Cl_2O_5	Cl_2O_3	H Cl	Fe	FeO_3	$[Fe_2]Cl_6$	$FeCl_2$
			Zn	$ZnCl_2$				Co	$[Co_2]O_3$	$CoCl_2$	Br	H Br O_3		H Br				
			Mg	$MgCl_2$				Ni	$[Ni_2]O_3$	$NiCl_2$	I	I_2O_5	ICl_3	H I				
			Ca	$CaCl_2$														
			Sr	$SrCl_2$														
			Ba	$BaCl_2$														

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We have frequently in the course of this lecture spoken of the constitution of molecules and of their constituent atoms, and it may interest you to learn something of the relative size of these portions of matter. As has been said, they are too small to be measured or weighed directly, but from certain considerations an approximate knowledge of their size has been gained. Thus Sir William Thomson has stated that if we were to take a drop of water and magnify it to the size of the earth the molecules composing the drop would then be no larger than cricket balls and no smaller than small peas.

M. Athanase Dupre' calculates that a cube of water having a side of .001 of a millimetre (or about six one hundred billionths of a cubic inch) contains more than 125,000,000,000,000,000,000 molecules.

We owe to Annaheim the discovery of a very ingenious and beautiful method for ascertaining the approximate weight of an atom of hydrogen. He weighed out .0007 grams of fuchsin (one of the aniline colors having for its formula $C_{20}H_{19}N_3HCl$), dissolved it in water and diluted the solution up to one litre. In each cubic centimetre there was therefore .000,000,7 grams of the fuchsin, and yet, when placed in a tube one centimetre in diameter, the color of the compound was distinctly seen. When a drop of this liquid was placed in a test tube and held over white paper it showed a distinct red color. Therefore the eye can distinguish .000 000 02 grams of fuchsin. But if we assume that each drop contains only one molecule of fuchsin, and it cannot contain less, then, since the molecular weight of fuchsin is 337.5, the maximum weight of the hydrogen atom is $\frac{1}{337.5}$ of .000 000 02 grams or .000 000 000 059 grams. The experiment before you illustrates Annaheim's method.

It is with portions of matter such as these that chemistry deals. Reference book, *Barker's College Chemistry.*

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LECTURE II.

CHEMISTRY.

[CONTINUED.]

Besides the symbols thus far described as being used in chemical notation, we find it advantageous at times to employ what are called diagrammatic formulas. In these the formulas of the molecules are enclosed in equal rectangles. These diagrammatic formulas represent the substances as being in the state of a gas under normal conditions, and they further show that the molecules of all substances when in this state occupy the same space.

This last is a direct deduction from Avogadro's law, which may be stated as follows: Equal volumes of all substances, simple and compound, in the state of a gas when under the same conditions of temperature and pressure contain the same number of molecules. Hence each of these molecules occupies an equal space.

It is true that, as these formulas are used, they represent a surface only, and, as we are dealing with matter which must have volume and hence occupy space of three dimensions, they must be regarded as only graphic representations of certain facts in the constitution of molecules. The same criticism will also hold true of the graphic or structural formulas which we often employ for showing the manner in which we suppose the atoms to be grouped in a molecule.

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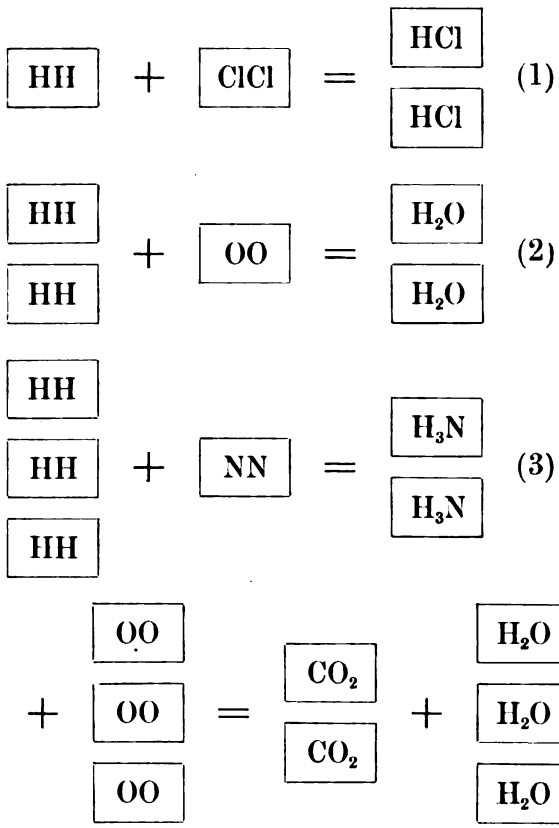
The use of diagrammatic formulas may be illustrated by the following examples:



These diagrams show immediately on inspection what volume of gases we will obtain when we know the volume of the substances taken. Thus from (2) we see that if we take two volumes of hydrogen and one of oxygen we shall obtain two volumes of water in the state of steam. From (4) we learn that if we burn one volume of alcohol vapor completely, three volumes of oxygen will be required, and two volumes of carbon dioxide and three volumes of steam will be produced.

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These diagrams are used but little, except for purposes of illustration, for, having once used them, we endeavor to bear in mind the fact that molecular formulas always represent the unit volume and equal volumes in the state of a gas.

It may now be well to inquire how the formulas which have been given as representing the molecular composition of these compounds have been derived. We will take water as an example. First, we make a qualitative analysis of it, which may be done as in the following experiment by passing a galvanic current through water and collecting the products. We obtain as a result two gases, one of which we recognize by proper tests as being oxygen, and the other as being hydrogen. Evidently water contains at least these two constituents. We then proceed to test this result by synthesis — that is we take hydrogen and oxygen and heat them up so that they may combine, and we obtain water as a result. Analysis and synthesis both show that water is composed of hydrogen and oxygen. The next step is to ascertain the amount of each element in the compound, and this is done by repeating the analysis and synthesis, taking weighed quantities of the material and carefully collecting and weighing the products, and as a result we find that water is composed of one part, by weight, of hydrogen to eight parts, by weight, of oxygen. We may, and have used many other means for analyzing and synthezing water and the result is always the same.

When we electrolyse water in a Hofmann apparatus, such as that before you, so arranged that we can collect and measure the separate products we see that the volume of the H obtained is about twice as great as that of the O. If we perform the experiment under the best conditions we find that the proportion, by volume, of

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H:O::2:1. If now we take the mass of that volume of hydrogen, which is equal to the volume of oxygen obtained, as unity, then the proportion, by weight, of H to O in water will be as 2:16. Letting H then represent the unit weight and volume of hydrogen, and letting O represent the unit volume of oxygen, and also 16 parts, by weight, of oxygen, we express the result of our experiments by the formula H_2O.

The example just given is a characteristic one, but the methods employed must necessarily vary with the substances under examination. Sometimes we easily obtain the ratio of the weights of the constituent elements in a compound, but are uncertain as to the weight of the molecule. If the compound can be converted into a gas the molecular weight can, however, be easily obtained by finding how much a given volume of the gas weighs as compared with that of the same volume of hydrogen, and this ratio, which is called the Vapor Density of the substance, is numerically equal to *one-half* the molecular weight.

We see if we admit that a molecule of hydrogen contains two atoms (and there are many reasons why we should do so) this relation of molecular weight to vapor density is a direct consequence of Avogardro's law. Thus let us take the following examples:

	HH	OO	ClCl	NN	HCl
M. W.,	2,	32,	71,	28,	36.5,
V. D.,	1,	16,	35.5,	14,	18.25,

	H_2O	H_3N	C_2H_6O	CO_2
M. W.,	18,	17,	46,	44.
V. D.,	9,	8.5,	23,	22.

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The vapor density may be determined by weighing equal volumes, as has been said, but if the compound is gaseous a speedier way for getting this value is by measuring its rate of diffusion. What is meant by diffusion is shown by this experiment in which we cause coal gas to diffuse through a membrane of porous earthern-ware. Now experiment has shown us that the velocities of Diffusion of gases are inversely proportional to the square roots of their densities. Thus take H and O:

For relative densities we have H:O::1:16.

For velocities of diffusion we have $H:O::\sqrt{16}:\sqrt{1}::4:1$.

Having explained, so far as our limits permit, the methods of notation and numeration employed in chemistry, and also the means by which we arrive at the information which our symbols and formulas seek to convey, we will next consider the system of Nomenclature employed.

On inspecting the list of elementary substances it is observed that there is no complete uniformity in the names applied among them; however we notice that a considerable number of them terminate in *um*. These are all regarded as metallic elements. The more commonly occuring and well-known metals are the only metallic elements which do not have this termination. Hence we may say that as a rule the metallic elements may be distinguished by the fact that their names terminate in *um*, while those of the non-metallic elements never terminate in *um*. It is of great assistance to be able to recognize these two classes of elements, because as we shall see they possess opposite functions as regards the part they play in combination. This difference becomes obvious when a compound substance is electrolyzed, for then the metallic element goes to the negative pole and the non-metallic element to the positive pole, and

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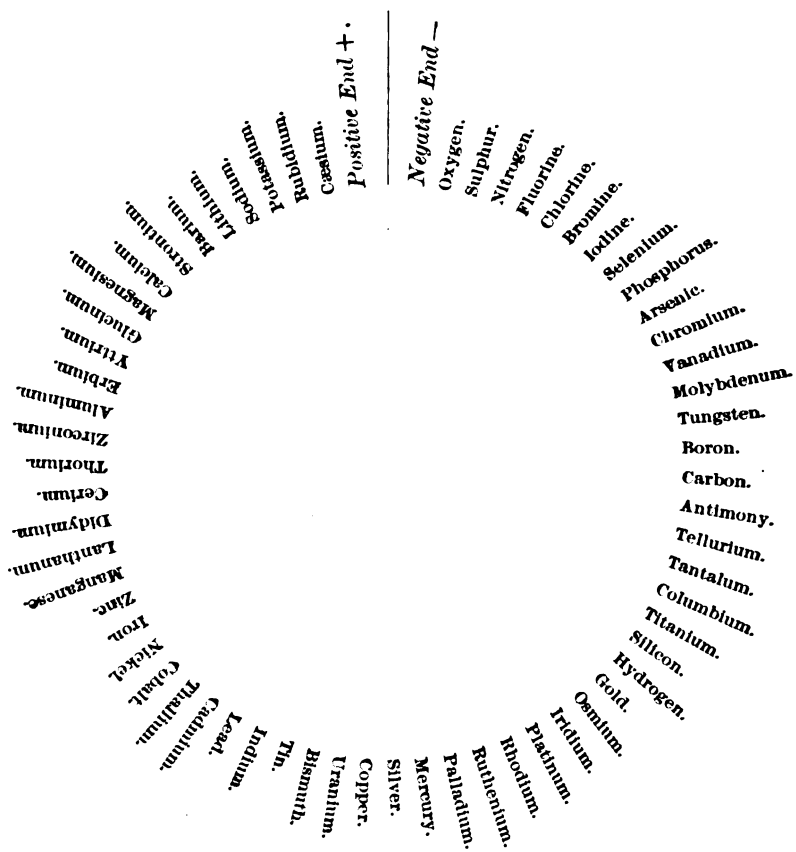
we may use these terms electro-positive and electro-negative as nearly synonymous with metallic and non-metallic. If we compare each element with all of the others we shall find that the elements may be arranged in a series such that if we begin with the most electro-negative and place them in rotation, beginning at the negative end, each element will be electro-positive to any element which precedes it, and electro-negative to any element which follows it. The following is such a list:

ELECTRO-CHEMICAL SERIES.



When we come to the naming of compound substances we find that these bodies may also be divided into two great groups, *e. g.*:

(1) Compounds whose molecules contain atoms of only two kinds, or which contain but two atomic groups. These are called Binary Compounds.

(2) Compounds whose molecules contain atoms of three different kinds, or which contain three atomic groups. These are called Ternary Compounds.

In fixing the names of the binary compounds we write the name of the characteristic element first and then the name of the other element, changing the termination of the latter to *ide*. Thus,

HCl	Hydrogen chloride
NaCl	Sodium chloride
H_2O	Hydrogen oxide
CaO	Calcium oxide.
CuS	Copper sulphide
AuI_3	Gold iodide
NCl_3	Nitrogen chloride.

Sometimes we have a group of elements which act like an atom of an elementary substance. Such a group is called a *radical*, and it may form a binary compound, notwithstanding that there are then three elements present. The names will thus be found as follows:

$(NH_4)Cl$	Ammonium chloride
Ag(CN)	Silver cyanide.

Sometimes we find two or more binary compounds formed by the union of the same elements, but a different number of atoms being taken. This can only result from a change in the valency of one of the elements. To represent this when there are but two compounds we write the name of the characteristic element first, giving it the ter-

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mination *ic* in that compound where it possesses the high valency, and *ous* in that compound where it possesses the lower valency, and change the termination of the other element as before. Thus,

FeO	Ferrous oxide
$[Fe_2]O_3$	Ferric oxide
$[Cu_2]Cl_2$	Cuprous chloride
$CuCl_2$	Cupric chloride
$[Hg_2]I_2$	Mercurous iodide
HgI_2	Mercuric iodide.

When there are more than two compounds of similar substances the two middle terms are designated as in the last case, while the compound in which the element of variable valency has a less value than in the lower of the middle terms is indicated by the prefix *hypo*, and the one in which it has a higher valency than the upper of the middle terms is indicated by the prefix *hyper*, or simply *per*. Thus,

Cl_2O	Hypochlorous oxide
Cl_2O_3	Chlorous oxide
Cl_2O_5	Chloric oxide
Cl_2O_7	Hyperchloric oxide.

These compounds are however often designated by numerical prefixes which are attached to the name of the element. Thus,

Cl_2O	Chlorine monoxide
Cl_2O_3	Chlorine teroxide
Cl_2O_5	Chlorine pentoxide
Cl_2O_7	Chlorine heptoxide.

On inspection of the ternary compounds we find that they comprise three large classes, viz., acids, bases and salts.

Acid molecules contain a characteristic non-metallic

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element or radical united to hydrogen by oxygen or its equivalent.

Basic molecules contain a characteristic metallic element or radical united to hydrogen by oxygen or its equivalent.

Salt molecules contain a characteristic non-metallic element or radical united to a metallic element or radical by oxygen or its equivalent. Salts are usually obtained by metathesis from acids and bases, but may be produced in other ways.

The names of the acids are formed by writing the name of the characteristic element or radical first, giving the suffix *ous* or *ic*, and the prefix *hypo* or *hyper*, according to the valency of this element, and then the generic name acid. Thus,

H_2SO_3	Sulphurous acid
H_2SO_4	Sulphuric acid
$HClO$	Hypochlorous acid
$HClO_2$	Chlorous acid
$HClO_3$	Chloric acid
$HClO_4$	Hyperchloric acid.

The names of the bases are formed by writing the name of the metallic element first, giving the suffix or prefix according to its valency, and then the generic name hydroxide. Thus,

$NaHO$	Sodium hydroxide
KHO	Potassium hydroxide
CaH_2O_2	Calcium hydroxide
$[Cu_2]H_2O_2$	Cuprous hydroxide
CuH_2O_2	Cupric hydroxide
FeH_2O_2	Ferrous hydroxide
$[Fe_2]H_6O_6$	Ferric hydroxide
NH_4HO	Ammonium hydroxide.

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The names of the salts are formed by writing the name of the metallic element or radical first, with the necessary suffix or prefix to indicate its valency, and then the name of the acid, from which the residue is derived, changing its termination when it is *ous* to *ite* and when *ic* to *ate*. Thus,

$NaClO$	Sodium hypochlorite
NH_4ClO_2	Ammonium chlorite
$KClO_3$	Potassium chlorate
$Ba(ClO_4)_2$	Barium hyperchlorate
$FeSO_4$	Ferrous sulphate
$[Fe_2](SO_4)_3$	Ferric sulphate
HNH_4NaPO_4	Hydrogen, ammonium, sodium phosphate.

We have said that salts may be formed by metathesis between acids and bases. Here are a few examples:

$$NaHO + HClO = NaClO + H_2O$$
$$KHO + HNO_3 = KNO_3 + H_2O$$
$$CaH_2O_2 + H_2SO_3 = CaSO_3 + 2H_2O$$
$$CuH_2O_2 + H_2SO_4 = CuSO_4 + 2H_2O$$
$$NH_4HO + HC_2H_3O_2 = NH_4C_2H_3O_2 + H_2O$$
$$NaHO + HC_3H_5O_4 = NaC_3H_5O_4 + H_2O.$$

From inspection of these equations we see that in each case a certain number of atoms of hydrogen in the acid have been replaced by atoms of the metallic element of the hydroxide. This property of the acid is called Basicity, and the number of atoms of hydrogen in the acid so replaceable is the measure of its basicity.

Acids and bases are distinguished by characteristic reactions and, as one of them, the reaction with litmus-paper is used as a test for acidity in gun-cotton, and, as also several instances have been brought to my notice of serious errors which have been made in applying this

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test, it has seemed wise to dwell upon it somewhat at length.

The material used in this test is a substance called Litmus which is a blue coloring matter extracted from a species of lichen. We obtain the dried extract in the form before you, and by simply boiling it with water and filtering the solution we obtain the substance in a form suitable for use. On pouring a little vinegar into this solution you see that the blue color is at once changed to red. So with nitric acid, sulphuric acid and muriatic acid we are also able to change the blue to red. This indicates an acid reaction. Substances which give an *acid reaction* change the color of litmus-paper from blue to *red.*

If we now pour into the red colored solutions ammonium hydroxide, or sodium hydroxide, or potassium hydroxide, or calcium hydroxide, the color of the solutions is changed from red to blue. The action of the ammonium hydroxide is most strikingly shown in this experiment called the Ammonia Fountain. Substances which give a *basic reaction* change the color of a litmus solution from red to *blue.*

These reactions are shown by electrolyzing a solution of Na_2SO_4 which has been colored with litmus. This neutral salt is decomposed as follows:

$$Na_2SO_4 + H_2O = 2NaHO + H_2SO_4.$$

And, as these bodies are separated at opposite poles, we get the basic reaction on one hand, and the acid reaction on the other.

For convenience in use we employ strips of paper, for our tests, which have been colored with such solutions. This is easily done by immersing strips of white bibulous paper in the solution. The paper sucks up the solution, and on drying it is colored blue or red according to the

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color of the solution in which it has been dipped. When dry, litmus-paper keeps for a long time unchanged. In making the test with it, it should always be *wet* with pure water. It should never be touched by the fingers since the secretion from the skin gives an acid reaction, as is shown by the following experiment. To detect the change in color the test paper should always be examined in a white light. This can be easily done by placing the wet test paper on a piece of clear glass.

In a shellacked room blue litmus-paper will always appear to have a reddish tint. The reason for this is, that blue litmus contains some red coloring matter, and experiments made at the Station have shown that, when using a spectrum, the same piece of paper appears blue when placed in the blue rays, and red when placed in the red rays. It is well, too, when examining a test paper for acid reaction to compare it with another piece which has been reddened by vinegar. Erroneous conclusions have sometimes been drawn from the fact that the color of a strip of blue litmus paper is sometimes changed by wetting it with water.

This reaction of litmus is so marked that it may be employed as a color test in quantitative analysis. The following experiment shows how we would use it when determining the amount of alkaline matter in gun-cotton.

The testing for acidity by the use of litmus-paper is as simple as any test in chemistry can be made, but, nevertheless, mistakes sometimes occur in applying it.

When we described the way in which chemical symbols were derived it was pointed out that the symbols represented definite weights of the substances, and that the same values were attached to them when they were combined into formulas. It becomes evident then that every chemical equation represents the proportions by weight

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of each substance which enters into and issues from a chemical reaction.

Since the symbols and formulas represent definite weights of matter, we are able to find, by calculation, either the percentage composition, or the number of atoms of each element it contains, or the atomic weight of each element, or the molecular weight, of any substance, provided we know three of the foregoing factors. For this purpose we may employ the following expression:

Let m represent the molecular weight of the substance,
a the atomic weight of any constituent,
n " number of atoms of that constituent,
x " per cent. of that constituent,
and 100 " total per cent. of the substance taken.

Then given the other factors to find x, the per cent. of one constituent present, we have

$$\frac{m}{na} = \frac{100}{x} \quad \text{or} \quad x = \frac{100na}{m}$$

By taking each constituent in succession we find the percentage composition of the substance,

e. g. What is the percentage composition of $CaSO_4$?

For Ca $n = 1, a = 40, na = 40$
" S $n = 1, a = 32, na = 32$
" O $n = 4, a = 16, na = 64$
" $CaSO_4$ $m = 136$

Solving for Ca $x = \frac{100 \times 40}{136} = 29.41$

Solving for S $x = \frac{100 \times 32}{136} = 23.50$

Solving for O $x = \frac{100 \times 64}{136} = 47.06$

Total, 100.00

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To find the formula of a compound when m, x and a are given, we have the expression:

$$n = \frac{mx}{100a}$$

And we find by its use successively the number of atoms of each element present in the molecule.

e. g. The molecular weight of quartz being 60 and its percentage composition being Si 46.67, O 53.33, find the formula for quartz.

$$\text{For Si } a = 28,\ x = 46.67$$
$$\text{“ O } a = 16,\ x = 53.33$$
$$m = 60$$

$$\text{Solving for Si } n = \frac{60 \times 46.67}{100 \times 28} = 1$$

$$\text{Solving for O } n = \frac{60 \times 53.33}{100 \times 16} = 2$$

$\therefore$ the formula of quartz is SiO_2.

To find the atomic weight of any constituent in a compound when m, x and n are given we have

$$a = \frac{mx}{100n}$$

e. g. The molecular weight of $AgNO_3$ is 170 and it contains 63.53 per cent. of Ag. Find the atomic weight of Ag.

$$a = \frac{170 \times 63.53}{100} = 108$$

To find the molecular weight of a compound when n, a and x are given we have

$$m = \frac{100na}{x}$$

e. g. Common salt contains 39.32 per cent. of Na, and

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it contains but one atom of Na. The atomic weight of Na being 23 find the molecular weight of common salt.

$$m = \frac{100 \times 23}{39.32} = 58.5$$

The above problems have been calculated for 100 parts of the compound substance. When any other quantity is taken as the unit

we let y = the quantity of the constituent
and z = " " " " compound

$$\text{and we have } y = \frac{naz}{m}$$

which we apply as before.

When equations are given, we may find the weight of any of the substances entering into or issuing from a chemical reaction as follows:

Let M = the molecular weight of the substance given,
W = " weight in grams or any other standard given,
m = " molecular weight of the substance required,
w = " weight in grams or any other standard required, then

$$\frac{M}{W} = \frac{m}{w} \text{ and } M = \frac{mW}{w}$$

and so on for each factor.

Reference books, *Barker's College Chemistry*, *Hofmann's Modern Chemistry*.

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LECTURE III.

COMBUSTION.

Among the more commonly occuring natural phenomena there is probably none with whose manifestations man is more familiar, and certainly none upon which he is more dependent in the civilized state, than that of combustion. Although this phenomenon has been familiar to man for ages, it is only for a comparatively short time that it has been recognized as a marked example of Chemical Change. As this phenomenon plays an important part in the changes attendant upon explosion, we propose to devote this lecture to the subject of combustion; the means by which it is set in operation and maintained; the substances which play a part in it; and the phenomena which attend it.

It is a matter of ordinary experience that a great difference exists among bodies as regards their combustibility. Thus phosphorus, sulphur, wood, coal, fats, oils and turpentine represent a class of bodies which burn with great readiness. These bodies are called combustible. Glass, earthen-ware, lime, granite and other rocks represent a class of bodies which do not burn. These bodies are called incombustible.

There are several means by which combustion may be started or, in common language, by which a body may be set on fire. Thus for instance, contact with a heated body, either solid, liquid or gaseous (such as a flame), friction,

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percussion, concussion, an electric spark, an electric current, thermal radiations, and chemical and physical changes may either of them set combustibles on fire or ignite them.

But, even when under the same conditions, we find that marked differences exist among bodies in the readiness with which they will ignite. This may be illustrated by placing a piece of phosphorus, one of sulphur and one of dry wood on the same cold iron plate, which is then heated by a flame. Very soon after the heat is applied the phosphorus ignites; after a much longer time the sulphur ignites; but it is only after a very long time that the wood can be made to ignite. The only difference which existed here was in the temperature of the plate, it being cold at first but getting hotter and hotter as the flame played upon it. Evidently then a comparatively low temperature is sufficient to cause the phosphorus to ignite; a higher one is necessary for the sulphur; and a still higher one for the wood. This difference holds good for all substances, and the temperature at which they ignite is called their Point of Ignition. Careful experiments have shown that this is a constant for each substance, provided the conditions remain the same.

When a combustible substance is ignited in free air it usually continues to burn until all the combustible material is consumed. Thus if we ignite this candle, combustion will continue until all of the candle has disappeared. If, however, we place a bell glass over the candle, so as to limit the amount of air with which it is supplied, we see that the flame grows dimmer and dimmer and soon is extinguished. This shows that the air plays a part in the combustion, and that, when only a limited amount of air is supplied to the burning body, the combustion can be maintained for only a limited

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time. The part which the air plays is evidently in furnishing some body which maintains the combustion, and the cessation of the combustion is as evidently due to the supply of that body having been exhausted.

Analysis of air shows that it is composed of oxygen and nitrogen in the proportions of about 1 : 4 by volume, and that the gases are physically mixed. On separating these and placing our burning candle, first in the nitrogen and then in the oxygen, we find that the candle is extinguished in the nitrogen, but that it burns with great brilliancy in the oxygen. It is evidently then the oxygen present which supports the combustion that takes place in air.

If we now return to the experiment in which the candle was burnt in a confined mass of air and examine the bell glass, we find that, while it was clear and dry when the experiment began, the inner surface is now bedewed with moisture. Let us hold another dry bell glass over a flame of hydrogen burning in the air, and again the cold walls of the bell glass are bedewed with moisture. Evidently then, through the combustion of these bodies in air, water has been produced, and this would only result from the chemical union of hydrogen and oxygen.

Let us now place in this jar a little clear lime water and shake it up. The lime water still remains clear. Now we will burn a piece of charcoal (one of the forms of carbon) in the air remaining in the jar and again shake the lime water up. This time the lime water becomes turbid through the formation of a milky precipitate, a reaction which we know to be due to the formation of CO_2. Evidently then the carbon of the charcoal and the oxygen of the air have united chemically.

What we have found to be the case here holds true of all instances of the burning of ordinary combustibles in

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air. The combustion is due to the chemical union which takes place between the atoms of these substances and of oxygen, and the heat and light, which result, are due to the impact of these atoms as they rush together. There is a fall of potential, and the result is the conversion of the mechanical energy into heat.

When bodies are burned in air it is likely that the ease with which combination can take must be somewhat interfered with by the nitrogen present, and that also a considerable part of the resulting heat must be expended in heating this nitrogen, hence if the combustion takes place in undiluted oxygen the phenomenon ought to be more marked and the display more brilliant. For these experiments we will produce the oxygen by each of the following reactions:

First, from mercuric oxide,

$$2HgO = 2Hg + O_2.$$

Second, from potassic chlorate,

$$2KClO_3 = 3KCl + 3O_2.$$

These bodies are decomposed, in the way shown in the equations, by simple exposure to heat. In fact, decomposition goes on so rapidly with the $KClO_3$, when it is once started that, in order to moderate its violence, we mix an equal weight of powdered manganese dioxide with the powdered chlorate.

Oxygen gas is now so extensively used that it may be obtained in commerce compressed in cylinders such as we have here. To fill our vessels with it we have simply to open the stop-cock and to allow it to pour in just as we would water from a spigot, for, as it is heavier than air, it drives the air out. We tell when the vessel is full by means of a stick such as this with a glowing coal on the end. When the vessel is full, the overflowing oxygen

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causes the stick held over the mouth to burst into flame.

In these two jars and the globe, which are now filled with oxygen, we will place ignited pieces of charcoal, sulphur and phosphorus, and you observe that the phenomenon of combustion is much more strongly marked than when these bodies were burnt in air. In this jar we place an ignited watch spring, and you observe that the iron burns as readily in pure oxygen as a splinter of dry wood does in air. Evidently then the combustion is much accelerated and intensified when the combustible is burned in contact with a supply of pure oxygen.

It is a commonly known fact that by subdividing or comminuting the combustible so that the air can be intimately mixed with it the combustion is accelerated. Thus we cut wood into shavings to enable the wood to ignite and burn more readily. This fact may be experimentally demonstrated by blowing this powdered combustible matter (starch) into a flame, or pouring this ignited powdered charcoal into this jar of oxygen. Now when substances are in the gaseous state they are very finely divided and can be intimately mingled with air or hydrogen, hence combustion goes on quite readily, as is seen in this gas flame, or in this flame which is produced by bringing hydrogen and oxygen together. The combustion in the latter case produces so much heat that we are able to burn this good sized file or to produce a very intense light by heating this piece of lime.

The effect of this very rapid combustion is seen when we mix coal gas and air together and fill soap bubbles with the mixture. On igniting the mixture the combustion proceeds so rapidly that a violent explosion ensues.

The explosion attending the combustion is still more strongly marked when we ignite a mixture of hydrogen and oxygen containing these substances in precisely the

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proportions in which they exist in water. This mixture can be easily obtained in just these proportions by electrolyzing water in the apparatus before you. The rapidity of combustion in the mixture is so great that the reaction takes place nearly simultaneously in all portions of the mixture, and hence the mixture has been styled Detonating Gas.

The ease with which detonating gas can be produced by electrolysis and the violence of its explosion has led Edison to suggest its use for torpedo purposes. For this use the acidulated water is to be enclosed in a hermetically sealed, stout, glass tube, in which is also sealed two platinum wires. By the passage of an electric current the water is electrolyzed, and as the gases are confined they exert a great pressure. If, having such an arrangement, we were now to pass a spark through the mixture explosion would result and an enormous pressure would be developed.

Of course, when other finely divided combustibles are mixed with air in the proportions best suited for their complete combustion, the reaction may also be so rapid as to result in an explosion. This mixing is most easily obtained with gases, but readily volatile liquids, such as the lighter petroleum oils, benzine, alcohols, turpentines, ethers and the like readily form explosive mixtures, and they have in fact been the cause of many serious accidents. Thus two British men-of-war, the *Doterel* and the *Triumph*, have been blown up, owing to the presence on board of a dryer for paints of which benzine formed a part; and the serious explosion in Pawtucket, R. I., and the still more disastrous one in Rochester, N. Y., arose from naphtha's having been permitted to escape into the sewers.

To produce explosive mixtures of solids and air it is

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essential that the solid should be quite finely pulverized and the particles well diffused through the air, but these conditions are easily obtained when combustible dusts are stirred up by a breeze, and (excepting recognized explosives) such mixtures have probably been the most frequent cause of accidental explosions. For example we have records of explosions of coal-dust laden air in coal mines, of sawdust in wood-working factories, starch in candy factories, flour in flour mills, rice in rice mills, and of dust in breweries and spice mills. Perhaps the most singular example of this class of explosions is that of finely powdered zinc which occurred at the Bethlehem zinc works in 1854.

If we consider and compare all of these cases of rapid combustion we see that we either have gases present or a mixture which closely approximates in state to that of a gas, and that the combustion is attended with the production of flame. It is by Inflammation that combustion is most readily propagated, and we shall see further on that this plays an important part in the combustion of solid mixtures.

Returning now to the experiments in which we burned charcoal, wood, sulphur, and the candle, in air and oxygen, you will recall that the solids disappeared and that gaseous compounds of C, H and S with oxygen, such as CO_2, H_2O and SO_2 were formed. This is our experience with common combustibles. It is obvious that, weight for weight, the gas, when under the same conditions of temperature and pressure occupies a much larger volume than the solid from which it is formed, so that these combustible solids must produce a volume of gas very many times greater than their own volume. But at the same time that the solid is converted into gas there is, as we have seen, a considerable development of heat also, and

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the effect of this is to increase still farther the volume of the resulting gas. The effect of heat in thus expanding gases has been measured, and it has been found constant for all perfect gases. Taking the volume of any given mass of gas at 0° C as the unit, it has been found that the gas increases or diminishes $\frac{1}{273} = .003665$ of its unit volume for every change of 1° C in temperature. This number .003665 is called the coefficient of expansion of the gas. Given this, and knowing the volume of any given mass of gas at a certain temperature, we can find what its volume will be at any other temperature, provided the pressure remains constant, by the following expressions:

Let V = the original volume,
V' = " new volume,
t = " number of degrees of change in temperature, we have when the temperature has increased,

$$V' = V(1 + .003665t),$$

And when the temperature has decreased,

$$V' = \frac{V}{1 + .003665t}$$

A simpler way is by applying Charles' Law. This law is that, when the temperature remains constant, the volume of any given mass of gas varies directly as its temperature on the Absolute Scale. Or,

Letting V = the original volume,
V' = " new volume,
T = " original temperature on the absolute scale,
T' = new temperature on the absolute scale,

We have $\frac{V}{V'} = \frac{T}{T'}$ and $V' = \frac{VT'}{T}$

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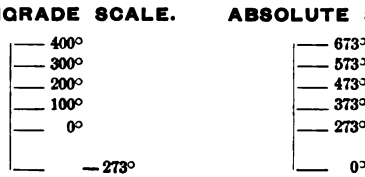
Knowing the temperature on the Centigrade scale, we find the temperature on the Absolute scale by adding 273 to the degrees Centigrade. The relation of the two scales is shown by the diagram:



As an example of the application of this expression let us take 15 cubic centimeters of O at 0° to find what the volume will be at 60°:

$$V' = 15 \text{ cm}^{-3} \qquad V' = \text{required}$$

$$T = 0 + 273 = 273 \qquad T' = 60 + 273 = 334$$

$$V' \frac{15 \times 333}{275} = 18.29 = \text{cm}^{-3}$$

If the change of state of the combustible bodies, which we have been considering, takes place within a confined space, it is evident that, since the volume of the products is much greater than that of the factors, a considerable pressure must be exerted upon the confining envelope. The extent of this pressure may be calculated, when we know the volumes of the factors and products, and the original pressure, by applying Mariotte's Law. This law asserts that for any given mass of gas, provided the temperature remains constant, the volume varies inversely as the pressure. Or,

Letting V = the original volume (at P),
V' = " new volume (at P'),
P = " original pressure,
P' = " new pressure,

We have $\frac{V}{V'} = \frac{P'}{P}$ or $P' = \frac{VP}{V'}$

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e. g. Let us fill a glass tube, of 18 $\overline{\text{cm}}^3$ capacity, with water, seal the tube, and completely electrolyze the water. What will the pressure on the tube then be?

Since we have taken 18 $\overline{\text{cm}}^3$ of water we have 18 grams of water, and knowing that one liter of H at 0° + 76 cm weighs .0896 grams, we can from the chemical equation, representing the electrolysis, calculate the volume, at 0° + 76 cm, which 18 grams of water will produce:

	2	$\boxed{H_2O}$	=	2 $\boxed{HH}$	+	$\boxed{OO}$
By weight,		36	=	4	+	32
By volume,		2	=	2	+	1

$$\text{The vapor density of } H_2O = \frac{18}{2} = 9$$

$\therefore$ 1 litre weighs .0896 $\times$ 9 = .8064 grams, hence the volume of 18 grams of H_2O at 0° = 76 cm will be $\frac{18}{.8064} = 22.32$ liters,

and, as by the equation, the volume of the products is to that of the water taken as 2:3, we have

$$x = \frac{3 \times 22.32}{2} = 33.48 \left\{ \begin{array}{l} \text{liters of the products} \\ \text{at } 0° + 76 \text{ cm.} \end{array} \right.$$

This volume is, however, reduced by the conditions of the experiment to 18 $\overline{\text{cm}}^3$ = .018 liters. Hence we have

$V = 33.48$ liters, $V' = .018$ liters

$P = 76$ cm, $P' =$ required

$$\therefore P' = \frac{33.48 \times 76}{0.18} = 141360 \text{ cm,}$$

or since an atmosphere = 76 cm

$$P' = \frac{141360}{76} = 1860 \text{ atmospheres.}$$

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We have called attention to the fact that during ordinary combustion heat is evolved, but it is to be expected that the quantity of heat for unit mass will vary with the substance taken. This quantity of heat, which a given mass of a given substance can evolve when burning under certain prescribed circumstances, is called its *calorific power*.

As has been said, this quantity varies very much with the nature of the substance burnt, but it is always constant for the same combustible, if burnt under precisely the same conditions, and it is also directly proportional to the weight of the combustible consumed. The following table gives the number of units of heat evolved by one gram of each substance when completely burnt (in its ordinary physical state) in oxygen gas:

Hydrogen,	34,462	Olefiant gas,	11,858
Wood charcoal,	8,080	Ether,	9,027
Diamond,	7,770	Alcohol,	7,184
Sulphur,	2,220	Phosphorus,	5,747
Carbon monoxide,	2,400	Dry wood,	3,654
Marsh gas,	13,063	Bituminous coal,	7,500

From these numbers we may calculate approximately the calorific power of any of our ordinary fuels, when we know their ultimate composition, if we assume that it is equal to the quantity of heat which would be developed by the perfect combustion of all the carbon, and of so much of the hydrogen present as is in excess of the amount necessary to form water with the oxygen which exists in the fuel. However, in estimating the available heat of a combustible, we must deduct the amount of heat required to convert this combined water (and also any hygroscopic water present) into steam at 100° as the temperature of the calorimeter, used in finding the quantities given above was 20°.

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If the products remain the same the calorific power of a given quantity of a given fuel is independent of the speed of the combustion, but it is evident, that, other things being equal, the resulting temperature will depend upon the rapidity with which the heat is developed as compared with the rapidity with which it is dissipated. If we assume, however, that all the heat is retained in the products of the reaction, we can calculate the maximum temperature which can be produced, provided we know the calorific power of the fuel and the specific heat of the products of the combustion. This temperature is known as the *calorific intensity* of a fuel.

Let W = the weight of the fuel burned,

" C = " calorific power of one gram of the fuel at 100°,

" W_1, W_2, W_3, etc., = the weight of the products of combustion,

" S_1, S_2, S_3, etc., = the specific heats ditto, then

$$W_1 S_1 + W_2 S_2 + W_3 S_3 + etc. =$$

the amount of heat necessary to raise the whole mass of the products through one degree, and hence,

$$\frac{WC}{W_1 S_1 + W_2 S_2 + W_3 S_3} = t,$$

which is the calorific intensity.

Having the data, let us now find what the pressure would be in the glass tube used in the last example, provided the gases existing there were detonated. We have

$$2\,\boxed{HH} + \boxed{OO} = 2\,\boxed{H_2O}$$

Or the 2 + 1 = 2 volumes,

Or the 35.48 liters are reduced to 23.32 liters,

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but at the moment of explosion heat is evolved, and to find the resulting temperature we have from above equation that

1 gram of H yields 9 grams of H_2O,

and, from the table,

1 gram of H yields 34,462 units of heat at 20° C,

hence, since 637 units are required to heat 1 gram H_2O from 0° to 100° and vaporize it, the available units of heat produced (at 100°) will be

$$34462-(617 \times 9) = 34462-5553 = 28909,$$

and the specific heat of aqueous vapor being .475, the calorific intensity will be

$$\frac{28909}{9 \times .475} = \frac{28909}{4.275} = 6762° \text{ C}$$

From above we find that the volume of the water vapor at 0° and 76 is 22.32 liters, then its volume at 6762° will be

$$V' = \frac{22.32 \times (6762+273)}{273} = \frac{22.32 \times 7035}{273} = \left\{ \begin{matrix} 575 \\ \text{liters.} \end{matrix} \right.$$

As, however, this volume is confined in a tube of .018 liters capacity, we have

$$P' = \frac{575 \times 76}{.018} = 2427778 \text{ cm.}$$

$$P' = \frac{2427778}{76} = 31944 \text{ atmospheres.}$$

We have seen that combustion ensues when a sufficiently pure combustible substance and a supporter of combustion are brought together in suitable proportions and are

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heated to the temperature at which chemical union takes place, and that, as a result of this combustion, heat is evolved and gases are produced; and, that, on account of the heat evolved, the gases produced are very greatly expanded if unconfined, but if confined they exert a very considerable pressure on the confining envelope.

When combustion is once started, in order to continue, it is necessary that the supply of both the combustible and supporter of combustion should be maintained, and that the temperature of these bodies should be kept at or above the point of ignition. The heat evolved by the burning mass tends to maintain the unburned portions of the mass at this necessary temperature, but, on the other hand, radiation, conduction and convection are continually operating to reduce this temperature.

For example, let us surround this candle flame with a coil of cold copper wire. The coil, as you see, does not touch either the wick or the candle, yet the flame is extinguished. Again, let us bring this piece of wire gauze down upon a gas flame, or let us so arrange the experiment that the gas passes through the gauze and is ignited above. In both cases you see that, while the cold gauze permits the gas to pass through, the flame is cut off. This is evidently due to the fact that the gauze absorbs heat from the flame and cools the gas, which passes through, below its point of ignition. This effect of the gauze is very strikingly shown when we pour a quantity of inflamed alcohol upon it. The alcohol runs through but the flame is extinguished.

This property of the wire gauze has been practically applied in the apparatus before you, which is known as Davy's Safety Lamp, and which is intended for use in mines where there is a possibility of meeting with explosive mixtures in the atmosphere. The lamp, as you see,

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is simply enclosed in wire gauze. When brought into an explosive or inflammable atmosphere the flame is very much elongated owing to the combustion of the materials which pass through the meshes, but in a still atmosphere the flame cannot be communicated with the atmosphere surrounding the gauze so long as the latter remains cool. As combustion goes on, however, the gauze may become heated to the point of ignition of the explosive mixture about it, and then it is, if anything, more dangerous than a naked flame. Another and more serious defect is found in the fact that, if the atmosphere is in motion with a velocity of eight hundred feet per minute and higher, the burning mixture within the enclosure may be driven through the gauze and ignite the exterior atmosphere.

The effect of the gauze in the above cases is explained as being due to the fact that it is a *good* conductor of heat, and so cools the flame. I have devised an experiment to test this. I take a bag of woolen cloth (a notably poor conductor of heat) and repeat the experiment with the burning alcohol, substituting the cloth for the wire gauze, and the result is as before. This experiment shows that the extinction of the combustion is due to the presence of a colder body. The advantage which the gauze possesses is that it can act efficiently for a longer time, and on a larger or hotter mass.

We have said that there were several ways by which bodies could be ignited. Let us before closing this lecture consider these ways:

1st. By contact with a heated body, either solid, liquid or gaseous. This is the ordinary way.

2nd. By friction. We have examples of this in the friction match and friction primer and it is also shown by the use of Munroe's apparatus for the conversion of mechanical energy into heat.

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3rd. By percussion. We have an example of this in the percussion cap. Or in the mixture of $KClO_3$ and P.

4th. By concussion. We have an example of this in the toy torpedo.

5th. By an electric spark. This is shown by the explosion of a mixture of H and O, and of an F igniter.

6th. By an electric current. This is shown by the explosion of a D. E. igniter.

7th. By thermal radiations. This is shown by the use of a "burning" lens.

8th. By chemical changes. This is shown by the action of H_2SO_4 + water on P. Or by igniting P, in contact with $KClO_3$, under water by the action of H_2SO_4. The service example is found in the Sulphuric Acid Fuze.

9th. By physical changes. This is shown in the "Fire" Syringe.

10th. By chemical and physical changes. This is shown in the Dobereiner lamp, in the coil of Pt wire, or by covering a bit of P with dry, powdered charcoal, or by saturating paper with a solution of P in CS_2.

Reference books, *Barker's College Chemistry, Cooke's New Chemistry, Bloxam's Chemistry, Faraday's History of a Candle Flame, Stewart's Heat, Ganot's Physics, Converse's Torpedo Fuzes.*

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LECTURE IV.

EXPLOSIVES—GUNPOWDER.

From the experiments made in the last lecture we saw that, if under certain circumstances a combustible and supporter of combustion were mixed and ignited, an explosion ensued, and that these circumstances seemed to be that the mixture should be so intimate, and the materials so pure, that the combustion could go on with great rapidity, and further, that the products of the combustion should occupy a very much greater space than the factors. We further saw, that if oxygen were supplied to the combustible, combustion could go on out of contact with air, and even in the midst of and in contact with a body of water, and that this oxygen might either be supplied in the free state, or combined, as in $KClO_3$, to be liberated as the combustion progressed.

The latter condition is that which obtains in the class of explosive mixtures of which gunpowder is a conspicuous example, and this is owing to the fact that we can thus obtain the explosive in the compact, convenient solid state which permits of its being worked into such forms and masses as will best fit it for the purpose to which it is to be applied. On consideration it becomes evident that there are a very large number of combustibles and a very large number of oxidizing agents which may be employed in making explosive mixtures, but long experience has led to the conclusion that a mixture of wood

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charcoal and potassium nitrate is the best adapted for use in ordinary guns. As, however, such a mixture possesses a relatively high point of ignition, it is necessary to add to it a portion of some substance possessing a lower point of ignition, and sulphur has been selected for this purpose.

On consideration, it becomes evident that, in such a mixture, the proportion of each substance used may be varied between quite wide limits, and yet each mixture may be explosive, but that there must be some one among them which is best adapted for use. Experience has led to the belief that a mixture containing

KNO_3 75 per cent, C 15 per cent, S 10 per cent

is mixed in the best proportions, and the majority of the military nations have adopted this mixture. Debus, in his masterly essay on the "Chemical Theory of Gunpowder,"* says: "If, therefore, the composition of a gunpowder is required which shall possess nearly the greatest energy, and at the same time contain the smallest amount of sulphur compatible with this condition, an experience extending over 500 years has selected a mixture which contains saltpetre, carbon and sulphur nearly in the theoretical proportions."

As gunpowder is a mechanical mixture, it becomes evident that, to secure uniformity in the product, the substances must be pure, finely divided and intimately mixed, hence we will now review the methods of production and preparation of the constituents, and the manipulation of the mixture.

The nitre or saltpetre used in the manufacture of gunpowder comes from two different sources. The first, known as India saltpetre, is potassium nitrate; the sec-

*Phil. Trans. 173, 523-594; 1882.

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ond, known as Chili saltpetre, is sodium nitrate. The names of the different saltpetres, India and Chili, are derived from the localities in which they are found in the largest quantities. The nitric acid, with which the metallic elements are combined, is either formed from the oxidation of organic matter in the soil, or from the union, under peculiar conditions, of the nitrogen of the air with the oxygen of the air. The India saltpetre is probably formed in the first way, the Chili saltpetre in the second. The India saltpetre is found either in caves or disseminated through the soil. When it is found in caves the rock is broken up by suitable means and mixed with pounded wood ashes. This latter is added to convert the calcium and magnesium nitrates, which are also present, into potassium nitrate. The mixture is then treated with water and allowed to stand until the impurities have settled. Then the clear supernatant liquid is decanted and evaporated until the nitre begins to crystallize. It then stands till all the nitre which will separate has done so, when the mother liquor is drawn off, and the crystals are dried and packed in bags for transportation.

The earth from which the nitre is obtained is found incrusted with it. It exists widely disseminated through the soil, and when the rain and dew, which fall, have filtered into the soil they dissolve the nitre. As the water rises during the day, owing to capillarity, it brings the nitre with it, and, when the water evaporates, the nitre is left as a white efflorescence. The soil is now gathered and treated in the same manner as the rock from the caves, except that, it is so rich in nitre, it is not necessary to mix wood ashes with it. Although it has been stated that the India saltpetre receives its name from the locality in which it is most abundantly found it is not to be inferred that it is not found elsewhere, for it

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is quite widely distributed over the earth, and in many places it is in sufficient quantity to be profitably worked.

In countries where the saltpetre is not produced naturally in sufficient quantity, the people resort to artificial means for obtaining it. This is briefly described by stating that the refuse of the stable and slaughter house is mixed with earth and ashes and piled in heaps where it can be exposed to the sun and air. The heaps are moistened, from time to time, in order to assist the change. After about three years the process is completed, and then the earth is treated in the manner previously described for the extraction of the saltpetre. In Sweden for a long while some of the revenue taxes were paid in saltpetre which was produced in this way.

The Chili saltpetre is found as an extensive deposit in the district of Tarapaca, Northern Chili. So great is the quantity accumulated there that it is estimated that, at the present rate of consumption, it would last 1,393 years. The nitre is quarried, just as other rocks are, by blasting, and the mass which is extracted is broken up and thrown into a boiler. Water is added and the whole is boiled until a saturated solution is obtained. The earthy matters and common salt which have separated are now taken out, and the clear liquid is drawn and run into coolers, where the saltpetre crystallizes out and is dried and bagged for shipment.

India saltpetre is often made by treating the Chili saltpetre with wood ashes, or with salts of potassium, by which means potassium nitrate is obtained and sodium carbonate or other salts of sodium result.

The sulphur used for gunpowder is principally of volcanic origin, and is found in a free state, mixed with impurities, in volcanic countries, such as Sicily, the Sandwich Islands, etc. Sicily furnishes the greater part of

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the sulphur of commerce. Its yearly product amounts to about 100,000 pounds. The sulphur is separated from its impurities by simple distillation.

The charcoal employed is produced by the destructive distillation of wood, the dry wood being packed in iron retorts which are heated by suitable means. As a result the cellulose is decomposed, all of the volatile matters being driven off and leaving the charcoal behind.

The powder manufacturers prepare their own charcoal, but the other materials are obtained in commerce and must be subjected to repeated processes of purification before they are suitable for use in this manufacture.

Thus the saltpetre of commerce contains impurities, such as common salt and sand, which would act injuriously if incorporated into the powder, and the sand, especially, would also endanger the lives of the workmen during the process of incorporation. The method of purification depends, first, upon the fact that saltpetre is much more soluble in hot than in cold water, while the impurities, if at all soluble, are not rendered more soluble by heating the water. The method depends, secondly, upon the fact, that, when the saltpetre crystallizes it separates from the impurities in the solution.

To effect this the crude saltpetre is dissolved in large copper pans capable of holding 500 gallons of water. Two tons of the nitre are put in and 270 gallons of water are added, the whole is then allowed to stand over night, and in the morning fires are lighted under them. At the bottom of the pans are false bottoms perforated with holes into which the sand and other insoluble impurities can fall. Just before the solution begins to boil these pans are withdrawn. Besides these insoluble impurities a scum consisting of organic impurities rises to the top which is skimmed off. To ensure the whole of this rising, gela-

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tine or glue is added to the mass, and it serves to coagulate the impurities. The salt is all dissolved and the boiling commences about two hours after the fires are lighted. The boiling is continued until all the scum rises to the surface. When it has been skimmed off the copper is filled with water. It is heated up to boiling, and the solution is then filtered. This is done by straining it through bags, and by this means the last of the impurities, which are undissolved, are removed. From here the solution runs to the cooler, a large, shallow flat trough of copper, where, if the solution is allowed to remain undisturbed, the saltpetre crystallizes out in the form of large prismatic crystals.

Since, however, it is necessary to have the saltpetre finely pulverized, ready for mixing, it is generally customary to agitate the liquid while it is cooling, and the result is that the salt crystallizes out in the form of a fine powder, known as saltpetre flour. As fast as the flour is formed it is removed and placed upon an inclined platform to drain, and this is continued until all the flour has been separated. The liquid remaining, known as the mother liquor, is used for dissolving a fresh portion of the crude salt. The saltpetre flour is placed in a tank and subjected to three washings. In each the crystals are covered with water, and it is allowed to stand one-half hour when it is drawn off. Each time the water becomes saturated with saltpetre, but it also carries off some of the common salt. The solution from the last washing is nearly free from common salt. All of these solutions are used again to recover the saltpetre from them. The flour is now dried and is ready for use in the mixture.

The sulphur of commerce is purified by distillation and melting, being finally obtained in the form of roll

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brimstone. These rolls are then crushed to a sufficiently fine powder under heavy rollers, and the powder is then sifted to obtain it of a uniform degree of fineness.

The charcoal which is used is made from either willow, alder, aspen or black dogwood. These woods have been in use for many years, and recent investigations have shown that the popular belief, that they were the best, was well founded, for they furnish light, easily burning charcoals which have scarcely any ash. The lightness of the charcoal is due to the fact that the wood grows very fast. Of all the woods mentioned, the willow grows the fastest, and it has been found to furnish the best charcoal. Since the quality of the powder is largely affected by the kind of charcoal used and the degree to which the charcoal has been burnt, this operation must be conducted with great care.

Small wood of about ten years growth is preferred. Alder and willow of this age will probably be four or five inches in diameter, dogwood about one. Great stress is laid on the cleanliness of the wood. It must be free from every trace of bark, hence it is cut in the spring when the sap is rising and when the bark can consequently be easily removed. The wood, after stripping, is stacked for a year or two until it becomes thoroughly air dried.

The completion of the burning of the charcoal is marked by the color of the gas flame which issues from the retort. If red charcoal is wanted the combustion is stopped while the gas yet burns yellow, but if black charcoal is wanted the burning is stopped when the gas begins to burn blue. The product of coal in the last case is about 25% of the wood put in. Provided the cylinders are hot, when the wood is put in, the burning is completed in two or three hours. The gases which are given

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off consist of hydrocarbons similar to what are found in coal gas. Another substance, called pyroligneous acid, is also evolved, and this is often of sufficient commercial value to warrant the manufacturers in saving it. This is done by simply condensing the escaping vapors, when the acid forms as a dark, disagreeable looking liquid. It is used extensively in printing dress goods. When this apparatus is used the workman must depend upon his judgment, based on experience, as to whether the wood has been burned sufficiently or not. If the temperature of the cylinders is 1,800° F. black charcoal is formed, if 500° F. red charcoal is produced.

Red charcoal is softer, more easily crushed to powder, absorbs water from the air more readily, and is more easily ignited than black charcoal. While red charcoal ignites at 640° F., black charcoal must be heated up to twice that temperature before it will ignite. Of course the gunpowders made from these different charcoals partake of the qualities of the charcoal. Gunpowder made from red charcoal ignites readily and explodes violently, the grains break down easily into dust, and it absorbs water very readily from the air and becomes worthless. The powder made from black charcoal has a higher point of ignition, the rate of its explosion can be more easily controlled, the grains are not liable to dust, and, if properly made, it does not absorb water very readily. Besides the gases and pyroligneous acid, which are given off, coal tar is formed, and unless great care is taken it runs back into the cylinder, becomes decomposed by the heat and forms a hard, black coal which is quite incombustible and is worthless for powder making. When the charcoal is cool it is carefully picked over by hand, and the selected pieces are then pulverized in a suitable mill.

The materials having been carefully prepared and pul-

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verized, the next processes have for their end the thorough mixing of the ingredients.

The mixing machine consists of a drum of gun metal which revolves at the rate of forty revolutions per minute. The bearings of the drum are hollow to receive a shaft which passes through them. On the shaft is a series of forty-four arms or fliers which just clear the interior of the drum. The shaft revolves in an opposite direction to and with twice the speed of the drum. The mixing is carried on for five minutes, and the mixture passes to the incorporating mill. The process conducted here is the most important of all. By incorporation is simply meant the long continued grinding together of the various ingredients, in order to mix them so intimately that none of the separate ingredients are visible to the naked eye, but the mixture appears as a homogeneous mass. Unless this be done perfectly, complete, mutual decomposition of the constituents of the powder by combustion cannot be expected. The powder then depends chiefly for its excellence upon the completeness and thoroughness of the incorporation. Provided the incorporating mill is sufficiently powerful and too much of the mixture is not employed, the incorporation is effected in a few hours, and nothing is gained by continuing the process, but, as imperfectly incorporated powder cannot fail to be of inferior quality and, as it is liable to foul the gun, it is best to continue the incorporation for some hours longer, and if the powder is thus rendered too violent, we can overcome this defect by making the mass very hard and dense, and by varying the size and shape of the grains.

The incorporating mill consists of a circular bed of iron or stone on which the mixture is placed. A vertical shaft rises through the centre of this bed, and this shaft carries

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a horizontal one, on the two ends of which heavy stone or iron wheels, called edge runners, are hung. These wheels rotate upon the horizontal shafts and, as the vertical shaft revolves, these travel in a circle around the bed. At the point on the bed where the edge runners touch, the motion of rotation and translation are transformed into a twisting motion like that of a muller, and the material in contact is thus very thoroughly mixed.

The edge runners are generally of iron or stone, weighing from three to seven tons and being from four to seven feet in diameter. One wheel is a little nearer the vertical shaft than the other. They are driven by water power. The wheels are so movable on the spindle that they can accommodate themselves to the varying thicknesses of the layers of powder.

To incorporate, fifty pounds of the mixture are placed on the mill-bed and slightly moistened, then the wheels are set in motion. If the wheels are of stone weighing $3\frac{1}{2}$ tons, and making $7\frac{1}{2}$ revolutions per minute, the incorporation is completed in $3\frac{1}{2}$ hours. If the wheels are of iron weighing 4 tons, aud making 8 revolutions per minute, $2\frac{1}{2}$ hours are required for cannon powder. Thus we see that we can easily estimate the capacity of a powder mill, if we know the number and size of its incorporating mills.

The workman does not remain in the mill throughout the operation, but only comes in occasionally to wet the charge. From two to ten pints of water are used, depending on the weather. When the operation is completed the mill cake, as the mixture is now called, is removed from the bed and runners by the aid of a copper chisel and wooden mallet. It is then tested by flashing to see that the incorporation is complete.

The chief danger during the manufacture of powder

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is in the incorporating mills, and it is fortunately located at this point, because there is less powder here at any one time than there is in any other part of the factory. To render the damage done by the explosion as slight as possible, the buildings in which the mills are put are built with a very strong framework covered with light boards, or else with three sides of stone and the other of light wood. When the explosion occurs the wooden side is blown out and the walls remain. As the mills are sometimes built in groups, to prevent the explosion of one wheel mill being communicated to another, a drenching apparatus automatically wets the charge in the mills adjacent to the one exploded.

Another plan for protecting the mills is by building barricades. At the Dupont Works these are huge masses of masonry filled with earth; at the Oriental Mills they are simply of wood built in the shape of an A. While these barricades serve in some measure to prevent ignited particles from being thrown from one mill to another, they would not probably prevent the transmission of vibrations or shocks from one mill to another.

The mill cake is partly in the form of fine meal and partly in the condition of cake, and it now passes to the press mill. This is a powerful hydraulic press with a rectangular box, which is divided into compartments, of the desired width, by means of moveable copper or gun-metal plates. When the spaces have been charged with the mill cake, pressure is applied, which results in causing the particles to cohere, and the powder is taken from the press in the form of sheets, having an area equal to that of the press plates and a thickness which is dependent on the filling space and the amount of pressure applied. Sometimes the press plates are corrugated like waffle irons, as for instance in the manufacture of Waffle

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and Hexagonal powders, and sometimes they are replaced by a press block filled with moulds, in each of which a separate grain is pressed. The latter form is used for modern large-sized grain powders such as Cocoa powder.

This operation is a very nice one, for the density of the finished product depends upon the pressing in this mill. Col. Brackenbury,* R. A., says of this: "Gunpowder is such a nervous and sensitive spirit, that in almost every process of manufacture it changes under our hands as the weather changes. Sometimes its sensibility can be detected and allowed for, as in the process of pressing it into moulds, when we can by actual trial tell what densities we are getting, and give more or less pressure as is required. For instance, on the morning of the 13th of June, 1882, the pressure had to be applied for 45 seconds. Later in the day only 29 seconds were required to obtain the same density, so that in the morning of a June day half as much again time was required as in the afternoon. On the 30th of June, 1882, during part of the day the time was as short as 26 seconds; on the 11th of December the time varied between 98 and 84 seconds to get the same density as was obtained in June. In the other stages of manufacture we have no such indications as in the pressing process, but it is a fact that not only the warmth of the summer and the cold of the winter affect it greatly, but the morning mists, the sunshine of midday, the dews of evening, yea, even a passing cloud, tell upon its nervous temperament."

The press cake passes to the corning or granulating machine where the cake is cut into grains. The corning machine consists of a hopper, into which the charge is fed, an elevating band, an endless revolving table, four

*Jour. Roy. United Service Inst., 28, 379; 1884.

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pairs of rollers, and several sets of screens for sorting the grains into boxes which are placed to receive the different sizes.

The rollers, which are of corrugated or toothed gun-metal, are adjusted to the size of grain required, the two upper being coarser than the two lower ones. When the hopper has been emptied a clutch is relieved which stops the machine, and, at the same time, rings a bell at the office, thus notifying the workman of the fact. As the machine is self supplying, the workmen are not obliged to be present during the operation of it.

The reel revolves for about a half hour, making forty revolutions, then one end is lowered, the head taken off, and the reel revolved backwards until all the powder has run into the barrel which is placed to receive it, from which it passes to the glazing barrels.

These are simply wooden barrels which revolve on a horizontal axis. By the friction of the grains against each other the angles are rounded off and a hard, polished surface is imparted to them, and thus they are in better condition for transportation. For the coarser cannon powder, and for blasting powder, an artificial glaze is added by putting a little graphite in the glazing barrel. The Oriental Powder Company use 4 oz. of graphite to 1,200 lbs. of powder, yet this amount is considered objectionable for fine grained regulation powder, since it retards ignition and fouls the piece. On the other hand, it is an advantage for powder to be used in fixed ammunition, since it permits the grains to pack close together.

During the process of glazing more dust is of course formed, hence the powder is again returned to the dusting reel and then goes to the drying house where it is exposed on shelves to a temperature of from 125° to 130° F. Here it is kept for about a day and is then ready for

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packing. When packed in quantity it is put in wooden kegs, which are held by wooden or copper hoops and fastened with copper or composition nails.

In 1862 or 1863, Col. G. W. Rains* introduced into the Confederate powder mills at Augusta, Georgia, a process of mixing which was claimed to be so much more thorough that the time required for incorporation was reduced three-fourths. The sulphur and charcoal were severally pulverized and bolted; the nitre (pulverized by disturbed crystallization) was added to these, and the mass, roughly mixed, was moistened with water and introduced into horizontal cylinders of sheet copper, 30 inches long by 18 inches in diameter. These cylinders revolved closely on a common axis consisting of a heavy brass tube 3 inches in diameter, perforated within the cylinders by a number of holes one-eighth inch in diameter. High pressure steam was introduced through this tube, raising the temperature to the boiling point, while the the water produced by condensation, added to that originally used to moisten the materials, reduced them to a semi-liquid slush, which was run out of the cylinders after about eight minutes rotation. On cooling, this mud became a damp, solid cake, the nitre, which in the state of boiling hot saturated solution had entered into the minutest pores of the charcoal, now recrystallizing. The cake so produced was tranferred to the incorporating mills, and, under 5-ton rollers, was in an hour brought to the condition of finished mill cake, ready to be cooled and granulated, while, without the steaming process, four hours incorporation in the mills had previously been necessary to produce powder of the same first-class character The capacity for work of the mills was thus practically quadrupled, the thorough saturation of the char-

*Am. Chem. Jour. 2, 423; 1881.

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coal with nitre being accomplished by the steaming, while it remained for the rollers merely to complete the mixture of the whole mass and give the required density to the mill cake.

The so-called Wiener powder, the invention of Colonel Wiener of the Russian Artillery, differs in its manufacture from the ordinary powder in the fact that all of the moisture is eliminated in the press mill, the mixture here being brought to a temperature of 240° F., the melting point of sulphur. In this manner, equal densities were obtained, but the resulting grains were very porous, and consequently had a great capacity for moisture.

To reduce the danger attendant on the manufacture of powder, Nordenfelt and Meurling have devised the following process: They first grind the carbonaceous matter to a very fine powder, and then prepare the sulphur for use by dissolving it in bisulphide of carbon. The solution is effected by the aid of a gentle heat in a water bath, and the evaporation of the bisulphide may be prevented by covering its surface with a layer of water. A saturated or nearly saturated solution should be thus prepared. The pulverized carbonaceous matter and the solution of sulphur in bisulphide of carbon are then thoroughly mixed together in a closed vessel containing a mechanical stirrer. When the mixture is complete, the solvent is evaporated or distilled off by the aid of a gentle heat. The vapor of the bisulphide is collected and condensed, so that the solvent may not be lost. According to the inventors, when the bisulphide of carbon is evaporated, the carbonaceous matter and sulphur remain intimately mixed, and each particle of carbonaceous matter is impregnated with sulphur, instead of as present, where the admixture is obtained by grinding, the particles of carbonaceous matter and sulphur being only me-

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chanically placed side by side. The saltpetre is prepared for use by dissolving it in water, the solution is added to the pulverized carbonaceous matter already impregnated with sulphur as described above, and the whole is stirred together in a mechanical mixer.

The Fossano or Progressive Powder, used in the 100-ton gun at Spezia, is made in the following manner: After passing through the incorporating mill, the mixture is pressed into a cake of a density of 1.79. The cake is then broken up into grains of about $\frac{1}{8}$ to $\frac{1}{4}$ inch in diameter, which are mixed with a certain quantity of fine grained powder, and the mass is again pressed to a mean density of 1.76. This second cake is finally broken up into tolerably regular grains about $2\frac{1}{2}$ inches in length and breadth by $1\frac{3}{4}$ inches in thickness, thus forming an agglomeration of two densities.

Besides the changes in the methods of manufacture noted, several changes in composition have been proposed and some of the materials suggested have given excellent results.

Among these is the proposition of Nordenfelt and Meurling to use hydro-cellulose as a substitute for the charcoal, while Prof. Karl Himly proposes to use hydrocarbons precipitated from solutions in naphtha as a substitute for both charcoal and sulphur. One advantage claimed for this last mixture is that it would be waterproof.

Various powders which are claimed to be smokeless have been devised. This is a property much to be desired in these times of enormous charges and rapid firing guns, but, so far as I have been able to learn, all of these powders contain a high explosive, and those best known are reported to be unstable.

The new powder which has attracted the greatest in-

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terest and been found most efficient in use is one of German origin, known as Cocoa or Brown Prismatic powder. Although this has been in successful use for a number of years, its composition is yet a trade secret, and hence the following report may prove of value. In considering it, we should bear in mind that many varieties of charcoal may be substituted for the charcoal mentioned there, and that other changes may be wrought at the pleasure of the manufacturer:

U. S. NAVAL ACADEMY,

ANNAPOLIS, MD., March 28, 1884.

SIR: In obedience to your order of January 21, 1884, I have the honor to report the results of my analysis of the Cocoa powder furnished me by Lieut. Comdr. Folger of the Naval Experimental Battery.

The powder was in the form of perforated hexagonal prisms, of the color of Cocoa, of a hardness of between two and three on Mohr's scale, and a density reported as 1.86 grams. Qualitative analysis showed the presence of potassium nitrate, sulphur, charcoal and water. The charcoal was of a reddish color and behaved towards alkaline hydroxides like under-burnt charcoal. The action was especially marked with ammoninum hydroxide as it dissolved out a marked quantity of humus-like substance. Water also yielded a marked amount of infusion. Quantitative analysis gave

	I	II	III	IV	Mean
Moisture,	1.05	1.10			1.08
Nitre,	80.52	80.36			80.44
Charcoal,	15.80	15.99			15.90
Sulphur,	2.19	2.26	2.24	2.28	2.24
					99.66

The charcoal contained,

	I	II	III	Mean
Carbon,	48.43	48.17	48.39	48.33
Hydrogen,	5.58	5.60	5.53	5.57
Oxygen,	44.64	44.93	44.75	44.77
Ash,	1.35	1.30	1.33	1.33
				100.00

It is to be seen by these analyses that the Cocoa powder differs markedly from the U. S. Regulation powder,

1st. In the proportions of the ingredients:

U. S. Regulation Powder,	
Nitre,	75.00
Charcoal,	15.00
Sulphur,	10.00
	100.00

2nd. In the character of the charcoal, which is red instead of black.

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In order to learn more of the nature of the charcoal, a partial analysis of the ash was made. The ash was red colored. It yielded,

Silicia,	13.93
Ferric oxide,	25.40
Alumina,	8.32
Lime,	28.50
Magnesia,	7.28
Undetermined,	16.57
	100.00

The presence of alumina in the ash seems to point to the club moss or some similar lycopodiaceous plant as the source of the charcoal. Thorpe says, regarding this, on page 168 of *Coal, Its History and Uses:* "The ash of modern lycopods is characterised by the large proportion of alumina which it contains, due in all probability to the free acids present in the roots, by which they are enabled to dissolve this earth from the soil, indeed so large a quantity of acetate and malate of alumina does club moss contain that an aqueous infusion of this plant was formerly used as a mordant in place of the ordinary 'red liquor' of the dyer. In no other plant, except in sphagnum, has this peculiarity of absorbing alumina been noticed. Direct observation has shown that the ash of trees such as the oak, birch and pine, growing on the same soil as club moss, is perfectly free from this earth." On page 169, he states, "Dr. Vohl has made observations on the distribution of inorganic matter of *sphagnum commune* during decay under water, which have a direct bearing on this point. He analyzed the ash of carefully selected moss, and subsequently allowed a portion to rot under water, and determined the nature and amount of the constituents in the water, and also those remaining in the plant:

	Original mass.	Decayed residue.	Aqueous solution.
Alkalies,	29.8	3.8	70.9
Ferric oxide,	6.4	13.4	0.2
Alumina,	5.9	28.7	3.2
Lime,	3.2	26.1	2.0
Magnesia,	4.9	3.2	1.3
Sulphuric acid,	4.3	6.0	3.2
Phosphoric acid,	1.1	3.4	0.5
Silicia,	41.7	15.0	17.5

It seems unlikely that moss should be used as a source of charcoal for this purpose, but it has been pointed out in my "Notes on the Literature of Explosives," *Proc. U. S. Naval Institute*, Vol. VIII, pp. 453 and 669, that peat, which is produced largely from the decay of moss, has been proposed for use in explosives.

Analyses of peat given by Thorpe, *loc. cit*, p. 172, are as follows:

	Carbon.	Hydrogen.	Oxygen and Nitrogen.
Dartmoor, Devon,	59.7	5.9	34.4
Lewis, Scotland,	61.2	6.1	32.7
Bog of Allen, Ireland,	61.0	5.8	33.2
Upper Shannon, Ireland,	61.2	5.7	33.1

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These results differ somewhat from the analyses I have obtained, as given above, but these just quoted, are calculated for ash free peat, while mine contains ash, and, besides, has probably undergone some treatment. Again, the chemical composition of peat will vary considerably with its age and the position of the beds in which it is found.

It occurred to me that it might be possible for a vegetable physiologist to determine something of the nature of the source of this charcoal from an examination of its structure by the aid of the microscope. With this in view I sent a portion of carefully washed charcoal from Cocoa powder to Dr. George L. Goodale, Professor of Botany at Harvard College, with the request that he should tell, if possible, whether it was of "phaenogamous or cryptogamous origin." No reference was made to any special plant. Under these circumstances the reply is somewhat surprising in its confirmation of the hypothesis suggested. It is as follows:

BOTANICAL GARDEN OF HARVARD UNIVERSITY,

CAMBRIDGE, MASS, Feb. 23, 1884.

DEAR PROFESSOR: I have been much interested in the specimen of charcoal sent by you. The very small amount of residue left upon incineration is suggestive of a cellular origin, *i. e.*, in distinction from a vascular. Even the best willow charcoal, or even that made from selected woods, will leave a trace of infiltrated matter and something in a form by which its source can be identified. But upon foil this left only an undistinguishable trace without any characteristic forms whatever. It behaves just like charcoal made by the Scotch process from large sea weeds, thoroughly leached and finely powdered. Peat-moss-charcoal and peat-charcoal have much the same character. It seems to me highly probable that this is made from a very clear peat (free from roots) or from sea weed treated as before stated. In the unburned coal I did not detect any diagnostic marks whatever, owing to the exceedingly fine comminution. The carbon which I send in this note is not very unlike that which you enclosed.

I wish I could be of use to you in this or any similar matter.

Yours very truly,

GEORGE L. GOODALE.

An analysis of the charcoal sent by Prof. Goodale gave the following result:

Carbon,	61.27
Hydrogen,	4.14
Oxygen,	32.27
Ash,	2.32

This charcoal was blacker than the Cocoa powder, and the ash was nearly white. The ash gave a marked reaction for alumina.

Respectfully submitted,

CHARLES E. MUNROE,

Professor of Chemistry, U. S. N. A.

To Commodore MONTGOMERY SICARD, U. S. N,,

Chief Bureau of Ordnance.

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It is remarkable that two observers, one testing by chemical methods, and the other by botanical, should have independently arrived at the same conclusion regarding the source of this charcoal, and a statement made in *Dingler's Poly. Jour.*, 263, *149*; 1887, tends to confirm this conclusion. The sample examined was made at the Rottweil-Hamburg, Powder Works, at Duneberg, and marked $^{C}/_{82}$. Lieut. Comdr. Folger reported, on trial, that it gave a fair initial velocity and low pressure, but fouled greatly. A peculiarity was that it burned so slowly that a grain could be held in the hand, lighted and then set down before the burning portion reached the fingers. With one grain weighing 42.4384 grams, the time of burning was 17 seconds. If powdered it still burns slowly as compared with pulverized *black* (regulation) powder, which shows that the slow combustion is not due to the great density and hardness only. The residue, when burnt in the open air, consisted of K_2CO_3 and K_2SO_4 only.

The Dingler article above cited states that charcoal made by the action of superheated steam on rye straw is used at Chilworth, Eng. Dupont has also succeeded in producing a brown powder which compares well with the foreign. His patents are cited at length in the *Proc. Naval Institute* 13, *582–586;* 1887, and it will be seen there that he uses baked wood, which retains its fibrous structures, and a carbohydrate, such as sugar, in place of the charcoal. He claims the following formula:

Saltpetre,	78 parts,
Sulphur,	2.8 to 3 parts,
Carbohydrates,	3 to 4 parts,
Baked wood,	12 to 12.5 parts.

We have frequently been asked to state to what the properties which distinguish the brown prismatic powder

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are due, and we trust it may not be considered out of place if we state our theory in this connection.

We hold that its property of imparting a high initial velocity to the projectile, while only exerting a relatively low pressure on the walls of the gun, is due to the action of a number of causes, viz:

1. The form of the grain. 2. The size of the grain. 3. The great density of the grain. 4. The great hardness of the grain. 5. The small percentage of sulphur. 6. The easy imflammability of the charcoal or carbohydrates. 7. The relatively great heat evolved. 8. The simplicity of the chemical reaction.

Cause 5 tends to reduce the readiness with which the powder will ignite, or raises its point of ignition, even when the grain is pulverized. Causes 1, 2, 3, 4 and 5 combined operate, so long as the first four exist, to produce a very slow rate of combustion. By the time, however, that the projectile is moved from its seat, the grains will be reduced in size and more or less broken up. We shall then have a finer grained powder which is highly inflammable at the temperature which exists, and consequently the volume of gas evolved will increase rapidly as the volume of the chamber increases. Owing to the relatively great quantity of heat evolved (cause 7), the cooling effect of the envelope is less marked than with other powders. As the chemical reaction is a comparatively simple one (cause 8), the speed of the reaction is probably more uniform than when the reaction is more complex, as in other powders.

According to Berthelot, dissociation plays an important part. This is possible, and even probable, with powders made from underburnt charcoal, as this contains carbohydrates, or with those in which a carbohydrate is a constituent of the mixture.

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The advantage of the form of grain employed was pointed out by Rodman,* the inventor, and his views have been confirmed by Sarrau.† The advantages of size, density (this is 1.86 in cocoa), and hardness are commonly known. Berthelot and Vieille‡ have shown that the hydrates of carbon, such as cellulose, contain an excess of energy above that given by the carbon and water which their decomposition would furnish. And Noble states,§ in his lecture on the "Heat-Action of Explosives," that a unit mass of Cocoa powder yielded a greater number of units of heat than any other of the standard powders, which Abel and Noble tested, yielded. He also shows‖ that the chemical reaction attending the combustion of Cocoa powder is simpler than that attending any other.

Among the practical difficulties which are met with in the use of gunpowder in ordnance, the erosive action on the bore is one which calls for serious attention. This action of gunpowder has long been recognized, even in the smaller calibres of great guns, but the very high charges now employed in modern ordnance (830 lbs. have been fired in a single charge from a 100-ton gun, and 300 lbs. from a gun not quite 25 tons in weight), and the relatively very long time during which the high pressure and temperature of the explosion are exerted, have aggravated to a very serious extent the evils due to erosion, and the consequent rapid wear of the bores of guns. In fact, with the enormous charges now used, the erosive action produced by a single round is distinctly perceptible.

The cause of this erosion has naturally been inquired into, and among the hypotheses which have been sug-

* *Experiments on Metals for Cannon and Cannon Powder, 291-297;* Boston, 1861.
† *Proc. Nav. Inst.* 10, *160;* 1884.
‡ *Proc. Nav. Inst.* 12, *187;* 1886.
§ *Heat in its Mechanical Applications, Inst. Civ. Eng. Lond., 211;* 1885.
‖ *Loc. cit. 209.*

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gested, the one which refers this action to the sulphur present has received credence. This does not seem unlikely, when we remember that we frequently have potassium disulphide, free sulphur and potassium carbonate among the products of the combustion of gunpowder, for it is a well-known chemical fact that a mixture of polysulphides of potassium and potassium carbonate, at a bright red or white heat, has a most powerful corroding action on metals (even on gold), and we might expect that this action on the iron or steel surface of the bore would vary with the temperature, pressure, time of cooling and the condition of the surface of the cylinder.

From experiments and observations made by Abel and Noble, it would appear that this was not the only cause or always the cause. Thus, with small charges, a particular powder containing no sulphur was found to exert very little erosive action as compared with ordinary cannon powder; but another powder containing the maximum proportion of sulphur tried (15 percent) was found equal to it under these conditions and exerted very decidedly less erosive action than it, when larger charges were reached.

This points to another cause, viz., that the erosion may be due to the flow of gases over the surface of the bore, these gases being highly heated and moving with a great velocity. As it has been found that the surfaces of the gun in contact with the charge are, at the moment of explosion, in a state of fusion, it can readily be understood how part of the surface may be scored off by this rapid flow of highly heated gas. This view is supported by experiments which I have made with gun-cotton on iron plates in which, under certain conditions, it has been found that the products of the explosion have exerted a marked eroding and puncturing effect. As there is no

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sulphur in this explosive, it is evident that this element played no part in producing the last described results.

The erosive action of the same powder, under the same temperature and pressure, will probably also be found to vary with the material of which the gun is composed. The more easily fusible the metal is, and the more readily it will combine with sulphur under the conditions which obtain, the greater will the erosion become. With the powder in use it has been found that the erosion could be diminished, though not completely prevented, by the suppression of the windage.

The gunpowder which gives the least erosion is that one which produces the largest quantity of gas while developing the least heat. With the same temperature of explosion, to avoid serious erosion, the pressure should be kept as low as possible.

The falling off in initial velocity, which has been observed in powders which have been stored for some time, has been attributed to an increase in moisture, but, from some observations which I* have made, I have been led to conclude that this is due to the chemical changes taking place within the powder owing to the presence of both moisture and air. I assume that the charcoal condenses the oxygen of the air in its pores, that this oxygen then oxydizes the S to SO_2, which by further union with the moisture and oxygen forms H_2SO_4, that this then decomposes the KNO_3, forming K_2SO_4 and HNO_3, and that this oxidation then proceeds again, the rapidity being increased with time. The presence of this inert K_2SO_4 must serve to retard the velocity of combustion. I have found this substance present in certain samples of powder, which had been subjected to an oxidizing agent, and I notice that Berthelot, and others, report the

*Proc. Nav. Inst. 9, 332-335; 1883.

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presence of this body in considerable quantity in deteriorated powders, although they have, as I have said, attributed the falling off in velocity to moisture.

We will now consider the chemical changes taking place during the explosion of gunpowder:

In the explosion of gunpowder, the oxygen of the nitre converts the carbon of the charcoal chiefly into CO_2, part of which assumes the gaseous state, whilst the remainder is converted into K_2CO_3. The greater part of the sulphur is converted into K_2SO_4. The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur and charcoal is resolved into a mixture of potassium carbonate, potassium sulphate, carbon dioxide, and nitrogen, the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effects of the explosion.

But, in addition to these, several other substances are found among the products of the explosion. Thus, the presence of K_2S may be recognized by the smell of hydrogen sulphide produced on moistening the solid residue in the barrel of a gun, and H_2S itself may be perceived in the gases produced by the explosion, the hydrogen being derived from the charcoal. A little CH_4 is also found among the gases, being produced by the decomposition of the charcoal, a portion of the hydrogen of which is also disengaged in the free state. CO is always detected among the products. It is evident that the collection for analysis of the products of explosion must be attended with some trouble, and that considerable differences are to be expected between the results obtained by different operators, from the variation of the circumstances under which the powder is fired and the products

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collected. When the powder is slowly fired, a considerable proportion of the nitrogen in the saltpetre is evolved in the form of nitrogen dioxide (N_2O_2), which is not found among the products of the rapid explosion of powder.

Some of the most recent experiments upon the explosion of gunpowder have been made by Noble and Abel under conditions very similar to those which occur in practice, the powder having been confined in a strong vessel of mild steel, in which the powder was fired by electricity so that the gaseous and solid products of the explosion remained within the vessel, and could be submitted to analysis.

Three samples of powder manufactured at Waltham Abbey were thus examined. Their composition is stated in the following table:

	Pebble Powder.	Rifle, Large Grain.	Fine Grain.
Nitre,	74.67	74.95	73.55
Sulphur,	10.07	10.27	10.02
Charcoal, viz, Carbon,	12.12	10.86	11.36
Hydrogen,	0.42	0.42	0.49
Oxygen,	1.45	1.99	2.57
Ash,	0.23	0.25	0.17
Water,	0.95	1.11	1.48
Potassium Sulphate,	0.09	0.15	0.36

The quantities of gunpowder exploded in different experiments varied from $3\frac{1}{2}$ ozs. to 1 lb, 10 ozs., and the pressures observed varied from 1 ton to over 36 tons on the square inch.

The solid products were found almost entirely collected at the bottom of the vessel, forming an exceedingly hard mass of a dark olive green color, exceedingly deliquescent, smelling strongly of hydrogen sulphide, and frequently also of ammonia. In some instances the solid residue was observed to become heated by exposure to

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air, from the rapid absorption of oxygen. The following table shows the proportions of solid and gaseous products furnished by each powder, when the ratio between the volume of the charge and that of the containing space was varied so that the maximum pressures attained were those stated at the head of each column:

	Pebble Powder.		Rifle, Large Grain.		Fine Grain.	
Pressure in tons per sq. inch,	1.4	12.5	1.6	35.6	3.7	18.2
Weight of solid products from 100 parts powder,	56.12	55.17	57.22	57.14	58.17	58.9
Weight of gaseous products from 100 parts powder,	43.88	43.83	42.78	42.86	41.83	41.92

The permanent gases generated by the explosion were found to occupy, at 0° C, and at ordinary atmospheric pressure, about 280 times the volume of the original powder.

The products of explosion furnished by 1 gramme of powder, were:

	Pebble Powder.	Rifle, Large Grain.	Fine Grain.
Potassium Carbonate (K_2CO_3),	.3258	.3415	.2861
" Sulphate (K_2SO_4),	.0710	.0844	.1252
" Sulphide (K_2S),	.1042	.0807	.0999
" Sulphocyanide (KCNS),	.0014	.0013	.0007
" Nitrate (KNO_3),	.0013	.0015	.0009
Ammonium Carbonate,	.0005	.0004	.0003
Sulphur,	.0445	.0490	.0381
Charcoal,	.0008	.0004	.....
Total solid products,	.5495	.5592	.5512
Carbon dioxide (CO_2),	.2685	.2630	.2689
" monoxide (CO),	.0477	.0422	.0355
Nitrogen (N),	.1123	.1117	.1123
Hydrogen Sulphide (H_2S),	.0111	.0109	.0101
Marsh gas (CH_4),	.0006	.0008	.0004
Hydrogen (H),	.0006	.0009	.0007
Oxygen, (O),	.....	.0002	.0003
Total gaseous products,	.4408	.4297	.4282

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From this table it appears that the solid residue of fired gunpowder consists chiefly of potassium carbonate and sulphate, with, usually, smaller proportions of potassium sulphide. The gases evolved are chiefly carbon dioxide and nitrogen, with a small quantity of carbon monoxide.

The great variation in the proportions of potassium sulphate and sulphide, coupled with our knowledge of the mutual relations of these bodies at high temperatures, would support the belief that the sulphate is first produced, and is partially converted into sulphide by secondary reactions.

The complex character of the decomposition, and its variation under different conditions, render it impossible to write a single general equation representing the explosion of gunpowder; but in order to illustrate the method of calculating the force of fired powder in any given case, we may take the following equation as a simple expression of the principal reaction:

$$4KNO_3 + C_4 + S = K_2CO_3 + K_2SO_4 + 2N_2 + 2CO_2 + CO.$$

The mechanical force exerted in explosion depends upon the production of a large volume of gas from a small volume of solid, the volume of the gas being increased by the expansive effect of the heat generated in the combustion of the charcoal and sulphur. To calculate the amount of this mechanical force, it is necessary to ascertain the volume of gas which would be evolved by a given volume of powder, and the extent to which the gas would be expanded by the heat at the instant of explosion.

It is calculated from the Table of Atomic Weights that

$4KNO_3$	=	101×4	= 404	grms.
C_4	=	12×4	= 48	"
S	=	32×1	= 32	"
		Gunpowder,	484	"

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While from the equation we find that this unit amount of gunpowder yields two molecules of N, two molecules of CO_2 and one molecule of CO. Remembering then that the molecular weight, in grams, of a substance has a volume of *22.32* liters at 0° and 76 cm., we have,

	Volume in liters at 0° and 76 cm.
$2N_2$	$= 22.32 \times 2 = 44.64$
$2CO_2$	$= 22.32 \times 2 = 44.64$
CO	$= 22.32 \times 1 = 22.32$
	111.6

Hence 484 grams of powder yield (in round numbers) 112 liters of gas under normal conditions.

To find the volume at the time of explosion, we have the heat of combustion, according to Abel and Noble, as 714.5° C, and the specific heats of the products, which have also been determined by experiment. The total specific heats of the products of one gram of powder, or $W_1S_1 + W_2S_2 +$ etc., will be,

	Weight.		Specific Heat.		Product.
K_2CO_3	.28	×	.2162	=	.0605
K_2SO_4	.36	×	.1901	=	.0684
N	.12	×	.2438	=	.0293
CO_2	.18	×	.2163	=	.0389
CO	.06	×	.2450	=	.0147
			Total,		.2118

and $\frac{714.5}{.2118} = 3373°$ is the calorific intensity,

then $V' = \frac{112 \times 3646}{273} = 1496$ liters,

or one gram of powder will yield $\frac{1496}{484} = 3.1$ liters.

In the ordinary charge of powder, one gram occupies a space of one cubic centimetre, but since, according to

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Abel and Noble, the fused solid products occupy one-third of the volume of the original powder charge the 3.1 liters of gas must occupy a volume of 67 $\overline{cm}^3$, hence the pressure developed will be,

$$P' = \frac{3.1 \times 76}{.00067} = 351642 \text{ cm.},$$

$$\text{or } \frac{351632}{76} = 4630 \text{ atmospheres},$$

or taking the pressure of 1 ton (2240 lbs.) per square inch as being equivalent to 152.4 atmospheres,

$$\text{we have } \frac{4630}{152.4} = 30.4 \text{ tons per square inch.}$$

The experiments of Noble and Abel gave 280 volumes of gas at 0° from one volume of powder, instead of 213.14 volumes, as required by the equation; then 280 volumes would become 3640 volumes at the temperature of the explosion, and would exert a pressure of 5460 atmospheres in the space available for the gas; this amounts to nearly 36 tons per square inch.

Variations in the proportions of the ingredients of gunpowder have less effect upon the total energy of the powder than upon its rate of burning. Thus, a slow burning powder containing a large proportion of charcoal will exert the same pressure in a closed vessel as is exerted by standard powder. For, when the proportion of carbon is large, more of the oxygen of the nitre is converted into carbon monoxide and less into carbon dioxide; and a given quantity of oxygen, when converted into CO, gives twice as large a volume of gas as when converted into CO_2. But the formation of CO_2, from a given weight of oxygen, developes 1.6 times as much heat as the formation of CO does, so that the thermal value of a powder varies inversely as the volume of gas measured at 0°;

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and the maximum pressure produced by the explosion is nearly the same for powders differing greatly in composition. This is illustrated by the results of Noble and Abel:

Powder.	Composition— Nitre,	Ch.	S.	Thermal value.	Gas at 0°.	Maxium pressure in tons per square inch.
Mining,	67	19	14	509	360	44
Military,	75	15	10	714	280	43

In calculating the pressure, it is supposed, of course, that the whole of the gas is evolved at once, and is immediately raised to the same temperature, conditions never fulfilled in small arms or in cannon, where the combustion of the charge is not instantaneous, but rapidly progressive; where the confining space is rapidly increased by the movement of the projectile long before the whole of the charge has exploded; and where the heated gas is cooled by contact with the metal of the piece.

The calculation given above can be regarded only as an illustration of the method, since there are several circumstances which vitiate the conclusion arrived at. The chemical equation, on which it is based, is confessedly imperfect. We know little or nothing of the real conditions of the products at the moment of the explosion; it is probably very different from that after cooling, when we examine them. From what is known of the effect of heat upon carbon dioxide and carbon monoxide, it is almost certain that these gases are at least partially resolved into their elements at the moment of explosion, and it is scarcely likely that the complex molecules of potassium sulphide and carbonate would exist at so high a temperature. Any breaking up of these molecules would increase the expansion, and render the above estimate of the force of fired powder too low.

If dissociation or temporary decomposition of the products occurs as a result of the high temperature, the acts

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of combination, which must take place during the expansion and consequent cooling, must be attended with evolution of heat, rendering the decrease of pressure more gradual than it would otherwise be.

The actual rate of expansion of gases at so high a temperature is inferred from our experience of their behavior at comparatively low temperature, and there are some indications of a want of agreement under the two conditions. The experiments of Andrews have shown that, even at a pressure of 100 atmospheres, carbon dioxide exhibits striking deviations from the law that the pressure exerted by a gas is inversely as it its volume.

Reference books, *Cooke's Ordnance, Simpson's Ordnance, Noble's and Abel's Researches on Fired Gunpowder, Debus' Theory of Gunpowder, Naval Institute Proceedings, Noble's Lecture on Heat-Action of Explosives, Bloxam's Chemistry.*

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LECTURE V.

CHLORATES AND NITRO-SUBSTITUTION COMPOUNDS.

We have pointed out that $NaNO_3$ is substituted for KNO_3 in the cheaper powders used in blasting, but we are not limited to these, for we can use other nitrates, such as the ammonium, barium or lead nitrates also, and indeed they have been used with considerable success. There is, however, a strong objection to the lead nitrate, viz., that it produces poisonous fumes, and this is so common a property that in countries such as England, where the government has sought by restrictive legislation to protect its people from the dangers attendant on the use or misuse of explosives, this salt is peremptorily prohibited for use in explosive mixtures.

We owe to Berthollet the suggestion that the nitrates in gunpowder mixtures might be replaced by chlorates, and he experimentally demonstrated the advantages and disadvantages which would result, and his suggestion has been availed of in the preparation of many mixtures.

But whilst the substitution of other nitrates for potassium nitrate in gunpowder is chiefly resorted to in order to reduce either the cost of the mixture or the brusqueness of its action, the chlorates or perchlorates are em-

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ployed in order to produce a more powerful explosive. On comparing the percentage compositions of these salts with the nitrates, thus,

	$KClO_3$	$KClO_4$	KNO_3	$NaNO_3$	NH_4NO_3
K	31.89	28.21	38.67	.....	.....
Na	.....	.....	.....	27.06	.....
Cl	28.96	25.47	.....	.....	.....
N	.....	.....	13.85	16.46	35.00
H	.....	.....	.....	.....	5.00
O	39.15	46.32	47.48	56.48	60.00
	100.00	100.00	100.00	100.00	100.00

we find that they contain less oxygen than the nitrates, and hence appear to be poorer oxidizing agents than the latter, but this difference becomes less apparent, if we remember that the chlorates yield all their oxygen contents, while with the nitrates, after decomposition, a portion of the oxygen still remains attached to the metallic radicle. The available oxygen is shown in the next table:

	$KClO_3$	$KClO_4$	KNO_3	$NaNO_4$	NH_4NO_3
KCl	60.85	53.68	.....	.....	.....
K_2O	.....	.....	43.03	.....	.....
Na_2O	.....	.....	.....	36.47	.....
H_2O	.....	.....	.....	.....	45.00
N	.....	.....	17.41	15.47	35.00
O	39.15	46.32	39.56	47.06	20.00

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Besides this the chlorate is decomposed at a comparatively low temperature (352° C), while oxygen is not evolved from KNO_3 until a red heat is reached, and too the combustion of bodies in contact with the chlorates results in the rapid development of a very high temperature.

According to Berthelot, a powder in which the nitre is replaced by an equivalent quantity of chlorate should have a heat of combustion greater by one-half than that of the gunpowder and, should possess double the force. The chlorate mixtures are very sensitive to friction and percussion, and they explode with great sharpness. The extreme facility with which they explode under a blow results from the low temperature at which decomposition begins, and from the high temperature which ensues from the combustion of the particles struck, and which heats the neighboring particles up to the temperature of decomposition. From the character of the explosive phenomena we conclude that the products of the combustion are very simple and stable binary compounds. The reaction may be represented by the equation,

$$3KClO_3 + 2S + 5C = 3KCl + 2SO_2 + 5CO,$$

which corresponds fairly well to a powder having the composition of

$KClO_3$,	75.00
S,	12.50
C,	12.50

The chlorate powders possess the disadvantage of eroding the walls of the gun in which they are fired, while the chlorine, sometimes liberated after firing, is very deleterious to those who are exposed to its action. The manufacture and handling is also attended with considerable danger. Besides, these powders are rather costly.

These disadvantages are not, as a rule, compensated

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for by the superior explosive power of the mixtures, but they are usefully employed in certain special applications, as, viz.: in the manufacture of fulminating primers and percussion caps.

The number of chlorate powders, which have been proposed, is quite large. Among these are the following:

Kellow and Short's (1866) Safety Powder—

Potassium chlorate,	12	6	10
Sodium nitrate,	30	36	10
Potassium nitrate,	8	4	20
Sulphur,	10	10	
Tan bark and sawdust,	46	50	46

The salts are dissolved in water and mixed with the tan and sawdust; the sulphur is then added and the mass dried. This preparation simply deflagrated with some difficulty when set fire to in the open air; but when tamped in the ordinary way it competed very fairly with ordinary powder. Preparations of a nature almost identical with it have been brought forward under the names Pyrolythe and Pudlorythe.

Knaffle's Powder—

Potassium chlorate,	46
" nitrate,	26
Sulphur,	15
Ammonium ulmate,	10

The last salt is obtained by dissolving ammonia in ulmic acid, the acid being produced by heating grape sugar with potassium hydroxide. The substances are powdered separately, mixed with a mucilaginous gum and reduced to the state of a paste, which is then granulated and dried with great care. It explodes violently under friction or blows.

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Spence's Powder—

	Cannon.		Musket.	
Potassium chlorate,	20	10	10	10
" nitrate,	....	....	....	0.25
Hydrogen sodium carbonate,	3 to 4	3 to 4	....	0.75
Sawdust,	7	3.5	....	.....
Charcoal,	2	1	2 to 3	1.25
Coal.	2	0.75	1	1.25
Wheat flour,	....	.....	2	2.5

The substances are treated with water and boiled, then dried by steam and granulated. The hydrogen sodium carbonate is replaced sometimes by potassium or lead nitrates.

Ehrhardt's (1865) Powder—

	Cannon.	Shell.	Blasting.
Potassium chlorate,	1	1	1
" nitrate,	1	....	1
Charcoal,	....	....	4
Tannic acid,	1	1	2

Sharp and Smith's (1866) Powder—

Potassium chlorate,	2
" nitrate,	2
" ferrocyanide,	2
" hydrogen tartrate,	1
Sulphur,	1

Some other comparatively safe applications have been made of potassium chlorate to the preparation of explosive agents for mining purposes, by only partly replacing saltpetre with it in mixtures, either of similar composition to ordinary gunpowder, or containing sulphides in addition to free sulphur. A substance called Tutonite, for which special advantages as a blasting agent have been claimed, appears to belong to this class of preparations. It possesses the peculiarity of being made

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up in the form of somewhat hard pellets or discs, instead of being in the granulated or pulverulent form.

Nisser's Powders—

Nisser patented in 1870 a mixture consisting of 55 to 60 parts of potassium chlorate and 45 to 55 of tartar, with a little potassium ferrocyanide.

Two mixtures proposed in 1866 contain

Potassium chlorate or perchlorate,	10.5	15.75
" ferro or ferricyanide,	1.5	2.25
" or sodium nitrate,	44.5	55.50
Vegetable matter,	6.5	10.00
Coal,	19.5	4.75
Sulphur,	15.5	9.50

Turpin's Powder—

Potassium chlorate,	20
Gas tar containing from 1 to 10% of an absorption substance such as infusorial earth,	10

One part of the chlorate can be replaced by permanganate.

An explosive recently patented in England by Dr. C. W. Siemens is a mixture of saltpetre, chlorate of potash and a solid hydrocarbon, and is considered suitable both for mining purposes and firearms. If ignited in the open air, the combustion takes place slowly and imperfectly, and therefore without danger. The incorporation of the ingredients is by preference effected as follows:

The saltpetre, chlorate of potash and hydrocarbon (for which may be taken paraffine, asphaltum, pitch, caoutchouc, gutta-percha, etc.) are mixed together in pulverulent form by passing through sieves or otherwise, and the mixture is then treated with a liquid volatile hydrocarbon, which acts as a solvent to the solid hydrocarbon. A plastic mass is thus produced, which is then formed

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into cakes or sheets by passing through rollers or otherwise, and which is rendered hard by evaporating the liquid solvent used, the sheets or cakes so produced being then converted into grains or pieces of any desired size, in the same manner as ordinary gunpowder. According to the inventor, this new mixture, which has about the same density as ordinary gunpowder, and is very hard, possesses with equal volume more than double the explosive force of the latter. The intensity of explosion can be regulated at will by varying the proportions of the ingredients and the size of the granules. These proportions should, generally speaking, be such that for each volume of the hydrocarbon, when converted into a gaseous state, there shall be present in the other ingredients three volumes of oxygen.

Melland's Paper Powder —

The following mixture is boiled for one hour in 79 parts of water:

Potassium	chlorate,	9
"	nitrate,	4.5
"	ferrocyanide,	3.25
"	chromate,	$\frac{1}{16}$
Charcoal,		3.25
Starch,		$\frac{1}{21}$

Strips of porous paper are then dipped in the liquor, rolled into the form of cartridges and dried at 100° C. To prevent their absorbing moisture they are given a coating with a solution formed by dissolving 1 part of xyloidine in 3 parts of acetic acid (density 1.04).

This paper is cheap, easy to make and fairly safe. It does not give off much smoke or leave much residue, nor does it erode the piece in which it is fired, while it is more powerful than gunpowder.

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The composition known as Powder Gas appears to be a modification of Melland's powder.

Abel* states that a similar paper powder was devised by the Messrs. Hochstader in 1860, and subsequently reproduced with slight modification by M. Reichen and that it was violently explosive when confined, but resisted detonation to a very high degree when submitted to percussion or friction.

†Sandoy's Pyronome and †Petry's Dynamogen are somewhat similar "paper" powders.

White Powders of Augendre and Pohl (1849)—

These are also known as German or American White Powders.

Augendre's original mixture was

Potassium chlorate,	50
" ferrocyanide,	25
Cane sugar,	25

The substances were moistened, mixed in bronze mortars, granulated and dried.

Pohl, who submitted Augendre's powder to many trials, modified the composition as follows:

Potassium chlorate,	49
" ferrocyanide,	28
Cane sugar,	23

being in the proportion of 3 equivalents of the chlorate to one of each of the others.

Pohl's statements as to the composition of the products of combustion may be represented as follows:

$$6KClO_3 + K_4FeC_6N_6 + C_{12}H_{22}O_{11} =$$
$$N_2 + 6CO + 6CO_2 + 11H_2O + 6KCl + 4KCN + FeC_2$$

From his calculations 100 grams of powder give 52.56

*Recent History of Explosive Agents, p. 96.
†Notes on Explosives, 5 and 7.

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grams of solid products and 47.44 grams of gas, which has a volume at 0° and 76 cm of 40680 $\overline{\text{cm}}^3$ and at the temperature of combustion (valued at 2604.5°C) a volume of 431162 $\overline{\text{cm}}^3$.

The conclusions which Pohl has arrived at, but which have never been verified, are all in favor of the White Powder. Sixty parts by weight, or 77.4 by volume, are equivalent to 100 parts of gunpowder, and they give but 31.35 parts of solid residue, where 100 parts of gunpowder, according to Bunsen and Schischkoff, give 68 parts. Besides, the temperature of the resulting gas is not so high for the white powder as for gunpowder, and hence a greater number of shots may be fired without heating the piece excessively. The ratio of this temperature to that of an equal weight of gunpowder is as .779:1. The estimation of the temperature is based on the hypothesis held as to the nature of the reaction and on the calculated temperature of the reaction, neither of which have been demonstrated exactly. If the process goes on precisely as Pohl believes, it is difficult to explain the erosive action of this powder upon guns from which it is fired.

Augendre and Pohl claimed other advantages for this powder, viz., it keeps perfectly in free air, inflames easily on contact with a spark, can be employed without being granulated, is simple to manufacture and is not very dear. According to Pohl, the manipulation of this powder presents absolutely no danger if the substances are pure and contain neither sulphur or carbon, and they cannot be exploded by a blow of iron on iron or by friction.

Experience does not confirm these assertions. Several instances of explosions are known to have taken place when the materials were mixed with great care; and a

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bottle filled with the powder has exploded when exposed to the sun in summer. According to Hudson, this powder may be exploded by the blow of a hammer on a block or stone, and it becomes more sensitive when the materials have been triturated in the moist state, owing, undoubtedly, to the more intimate and uniform mixture which is thus obtained.

It has not then been demonstrated that the manufacture of the white powder is exempt from danger, but, on the other hand, it has not been subjected to careful and searching trial. Zaliwsky proposed (in 1870) a mixture of potassium chlorate with oxalic acid, to which is to be added sulphur, carbon and analogous substances. This suggestion is worthy of trial.

If the undoubted dangers, which exist in the use of white powder, were overcome, still the erosive action which it exerts on the gun would tend to proscribe it for this use.

Uchatius has shown, by the aid of his eprouvette, that white powder is eminently brisante. From a ballistic point of view .093 grams of this powder are equivalent to 1.82 grams of Austrian cannon powder—that is, the two charges communicate the same initial velocity to projectiles of the same weight, but the pressure exerted on the bottom of eprouvette were 839 atmospheres for white and 458 atmospheres for the black.

As the erosive action of the powder is most marked on cast iron and steel guns, it was proposed to confine its use to bronze guns and to the charging of shells, for which it seemed especially appropriate. According to Hudson, they place glass bulbs filled with concentrated sulphuric acid in the shell together with the white powder, and the shock of impact, when the shell strikes the object to be destroyed, suffices to break the bulb and pro-

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voke the inflammation of the powder in contact with the acid. The method of exploding certain contact torpedoes is based on the same principle; the charge is composed of black powder, and this is fired by means of sulphuric acid and white powder.

A practical application was made of this powder by Shaw when building the piers at League Island. He arranged his pile-driver so that as the hammer fell it exploded a cartridge of this powder, and this explosion not only drove in the pile, but forced the hammer back again. The work was thus greatly accelerated.

A white powder similar to that of Pohl's has been known in England under the name of Reveley's powder.

Hafenegger's Powders—

Hafenegger has patented in England 6 species of powder analogous to Augendre's.

Potassium chlorate,	9	2	4	4	1	11
" ferrocyanide,	.....	1	1	.....	....	.....
Sulphur,	0.25	....	.....	0.25	....	0.25
Charcoal,	0.25	....	0.25	0.25	....	0.25
Sugar,	.....	1	1	4	1	.....

Hahn's Powder—

Potassium chlorate,	367.5
Antimony sulphide,	168.3
Charcoal,	18
Spermaceti,	46

The three last substances are mixed together, and the chlorate is added at the moment when the powder is to be used.

Horsley's Powder—

Potassium chlorate,	9
Nutgalls pulverized,	3

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The mixture is not granulated. The tests of this powder in Austria for use in muskets were not satisfactory.

Callou's Powder —

This is a blasting powder containing potassium chlorate mixed with orpiment (arsenic trisulphide).

Oriental Powder —

This consists of potassium chlorate and gambier.

Pertuiset's Powder —

This consists of potassium chlorate and sulphur, and is used in explosive bullets.

The development of these chlorate mixtures has been retarded, if not prevented, by the excellent results which have been attained with the very powerful explosive compounds.

The explosive substances, thus far treated of, have been produced by mixing together combustible matter and oxidizing salts. The next step in the development of explosive substances is reached when, by chemical means, we introduce our oxidizing agent into a chemical molecule which is composed chiefly of atoms which have a strong affinity for oxygen and form with it, under suitable circumstances, very stable and permanent substances. It is evident that by this means a greater degree of intimacy is attained.

This combination with hydrocarbon groups may be effected through the agency of the oxides of nitrogen, and it may result in the formation of two classes of compounds, viz., nitrosubstitution compounds, in which the nitrogen oxide is directly attached to the carbon atoms, and nitric ethers or esters, in which the nitrogen oxide is connected to the carbon atoms through the interposition of oxygen atoms.

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One of the best examples of the first class is picric acid, which was discovered by Hausmann in 1788. He made it by acting on indigo with nitric acid. In 1795, Welter prepared it by acting on silk with nitric acid. Stenhouse found an abundant source of it in the "Xanthorrhœa saxtilis," which was imported in considerable quantities from Botany Bay. But the cheapest and best source is from the action of nitric acid on phenol or "carbolic acid," which is itself produced from coal tar. Since this source has been discovered picric acid has become an important article of commerce and forms one of the cheapest and most brilliant of yellow dyes.

Laurent was the first to point out that picric acid could be derived from phenol, and that its formula should be $C_6H_2(NO_2)_3OH$, the reaction for its formation being

$$C_6H_5OH + 3HNO_3 = C_6H_2(NO_2)_3OH + 3H_2O.$$

It is a nitro-substitution product. It may be prepared experimentally by putting two teaspoonfuls of fuming nitric acid in a glass flask of 150 cm. capacity and adding cautiously, and in small portions, half a teaspoonful of crystallized phenol. The reaction is very violent and is attended with the copious development of nitrous fumes. When the action has subsided and the flask is cold, yellow crystals of picric acid will be found in the liquid.

It is made, commercially, by melting carbolic acid and mixing it with strong sulphuric acid, then diluting the sulpho-carbolic (or "phenol-sulphuric") acid with water, and afterwards running it slowly into a stone tank containing nitric acid. The mixture is allowed to cool, when the crude picric acid crystallizes out, the acid liquid (which contains practically no picric acid, but only sulphuric with some nitric acid) being poured down the drains. The crude picric acid, after being drained, is

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transferred to the "boiling stones," where it is dissolved in water by the aid of steam and afterwards allowed to cool, when most of the picric acid crystallizes out. The "mother liquor" is then transferred to the precipitating tank, in which the picric acid still left in solution is precipitated by the addition of sulphuric acid. The picric acid left in the "boiling stones" is once more dissolved in hot water and this second solution transferred to the crystallizing tank, where it is left to cool and where the picric acid crystallizes. These tanks generally contain about 130 lbs. of picric acid.

Finally, the picric acid, after draining in the tank, is transferred to a centifugal machine to remove the excess of moisture, and then dried on glazed earthen-ware trays in a steam-heated stove in which the temperature is not allowed to rise above 100° F.

According to Hill and Abel, picric acid does not explode, but, when heated, it burns sharply and quickly with a bright flame. Desortiaux states, that when heated slowly it vaporizes without undergoing any decomposition, but, when heated brusquely to a temperature a little above 300°, it explodes with violence. The explosiveness of picric acid has recently attracted notice, owing to an accidental explosion which occurred at Roberts, Dale & Co.'s Chemical works, near Manchester, Eng., June 22, 1877. The explosion was a very severe one, the local effect being as great as that produced by the explosion of 13½ tons of gun-cotton in the great Stowmarket explosion of August 11, 1871, and more marked and widely extended than in the case of the explosion of five tons of gunpowder in the Regent's Park explosion of 1874.

Inquiry showed that the company were large mauufactures of picric acid and other chemical compounds, and

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that before the explosion there was from 13 to 15 cwt. of picric acid on hand at the point of explosion, part of it being wet, and Colonel Majendie* is of the opinion that this, in conjunction with some of the metallic nitrates present was exploded, and that the explosion originated by fire.

In the course of this inquiry great differences of opinion were found to exist as to the explosiveness of picric acid, the books stating it to be explosive by heat, while the various manufacturers claimed that it could not be exploded in this way even in large masses, and they supported their claim by citing instances where as many as five or six hundredweight, packed in bulk in a dry cask of light wood, and exposed to fire had burned away without explosion. The experiments made on this point by Sir F. Abel, Dr. Dupre' and Col. Majendie gave results which supported the views of the manufacturers, yet Col. Majendie is not prepared to go so far as to assert that under no circumstances can unconfined picric acid be exploded by the action of fire.

There exists no doubt, however, that picric acid is liable to be exploded by detonation or by a blow, and that the picrates and the mixtures of picric acid, with oxidizing agents, are highly explosive. So far back as 1873 Sprengel remarked that "picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxidizers, a powerful explosive when fired with a detonator. Its explosion is almost unaccompanied by smoke."†

Apart from this inquiry, the detonation of picric acid has recently attracted interest from the alleged use of this substance by the French government in a particular fused and consolidated condition, as an explosive, under the name of *Melinite*, and an English patent (No. 15,089,

*Report H. M. Inspectors of Explosives No 81, Aug. 15; 1887.

†Jour. Chem. Soc. 9, 803; 1873.

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Dec. 8, 1885) has been taken out by Mr. A. M. Clark on behalf of M. Eugene Turpin of France, which claims the employment "as an explosive agent for military or other uses of the trinitrophenol, or picric acid, of commerce, unmixed with any oxidizing substance," by the use of a powerful fulminate detonator, or by the use of an intermediate priming of picric acid in powder, primed by the fulminate, or by dispensing with the fulminate and employing a sufficiently large charge of ordinary quick-burning powder enclosed in a strong tube and made to burst inside the charge of picric acid.

The explosiveness of picric acid, by detonation and by a blow, was also experimentally studied by the gentlemen above mentioned, and they find, 1st. That dry picric acid may be perfectly detonated by means of a 5-grain fulminate detonator. 2nd. That the detonation of a small quantity of dry picric acid is capable of detonating a quantity of picric acid placed at a short distance from it; and 3d. That the detonation of picric acid containing, at any rate, as much as about 17 percent of water may be effected by detonating a charge of dry picric acid alongside it.

The experiments on the effect of blows showed that, when thinly spread, dry, powdered, cold picric acid will be exploded by a weight of 54 lbs. falling 20 feet, and may be by a weight of 1 lb. falling 26 inches. The sensitiveness greatly increases with warming, so that, when near its melting point (say 240° F), a weight of 1 lb. falling 14 inches will explode it. It was easily exploded in this state by the blow of a light hammer (14½ ozs. with handle) on an anvil.

Berthelot* has also recently studied this subject, and he confirms the statement of Desortiaux and finds the

*Comptes Rendus. 105, 1159; 1887.

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same properties to obtain for the nitro-benzenes, nitro-napthalenes and the like, and he concludes: "Should a nitro-compound, such as picric acid, while burning in large masses, happen to heat the sides of the containing enclosure to a degree sufficient to induce incipient deflagration, the deflagration might combine to further increase the temperature of the enclosure, and the phenomenon might, occasionally, be transformed into a detonation. It would even suffice that the detonation should occur in an isolated point, either during a fire, or owing to the local overheating of a boiler or apparatus, to enable it to originate the explosive wave and propagate itself by influence throughout the whole mass, causing a general explosion.

A large number of the compounds called picrates are known, but the potassium and ammonium picrates are the only ones that have been much used in explosive preparations. They are all, except the ammonium picrate, readily exploded with more or less violence by heat or blows.

This is partially explained by inspection of the following table, which shows that they all contain sufficient oxygen to convert the carbon and hydrogen contents of the phenyl group into carbon monoxide and water. But they vary in the amounts of oxygen required for complete combustion, according to the amount of oxygen retained by the metallic radical. According to this view, since the H of the NH_4 consumes the most oxygen, the ammonium salt is the least sensitive, while the anhydrous barium salt is the most sensitive and powerful of any of those in the table. But this last body, in the crystalline state, contains water of crystallization, and hence falls below the potassium salt. We should infer that salts of unoxidizable metals or univalent ones of high atomic

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weights, if anhydrous and permanent, would be very sensitive and powerful.

Oxygen Required to Oxidize Picric Acid and the Picrates.

	Ammonium.	Acid.	Calcium.	Sodium.	Potassium.	Barium.
C	29.27	31.44	29.03	28.68	26.96	24.28
H	2.44	1.31	.80	.80	.75	.68
N	15.73	18.34	16.94	16.74	15.73	14.17
O	45.53	48.91	45.16	44.62	41.95	37.77
1	45.51	48.88	45.11	44.64	41.95	37.81
2	13.04	3.52	3.23	3.23	2.98	2.70
3	58.55	52.40	48.34	47.87	44.93	40.51

(1) Oxygen required for combustion of all contained C to CO and of all the phenyl H to H_2O.
(2) Oxygen required for oxidation of the basic radical, the H of the NH_4 being supposed burned to H_2O.
(3) Total oxygen required.

Owing to the fact that the contained oxygen is insufficient for combustion, mixtures with various oxidizing agents have been proposed. Thus,

Borlinetto (1867) recommended for blasting powder—

Picric acid,	10
Sodium nitrate,	10
Potassium chlorate,	8.5

This formed a quite sensitive powder.

Potassium picrate, $C_6H_2(NO_3)_2OK$, is one of the most violently explosive of the picrates. It is made by mixing warm potassium carbonate with a boiling solution of picric acid in water. On cooling, the liquid deposits small crystalline needles of a golden yellow color which show green and red colors by reflected light.

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When mixed with oxidizing agents, and especially potassium chlorate, its explosive properties are very much increased. Indeed, this mixture, with potassium chlorate, approaches very nearly to nitroglycerine and guncotton in violence, but it is so sensitive to friction, percussion and shocks as to be practically useless. Mixtures containing potassium picrate have been made the subject of experiment, especially in Paris where the so-called "Picric Powder" was prepared and experimented with upon a considerable scale.

One of these, Fontaine's Powder, composed of potassium picrate and chlorate, was intended exclusively for charging shells and torpedoes, but it was very dangerous to manipulate, and a fearful accident which occurred in Paris in 1869 during its use led to its being abandoned. Comparative experiments between this mixture and gunpowder as bursting charges for shell were made in England. When a shell weighing 16 lbs., 1 oz., filled with powder, was burst, all the fragments were readily recovered; they amounted to eighteen, including the plug of the shell, and of these, twelve weighed above 8 oz. and under 2 lbs., and only one fragment weighed less than 1 oz. Upon bursting a shell of the same kind and weight, filled with a mixture of potassium chlorate and potassium picrate, 100 fragments were recovered, and these weighed altogether less than 2 lbs., 6 ozs., nearly 14 lbs. of the shell have been dispersed in fragments too minute to be collected individually. Only one of the fragments weighed more than 8 ozs., and ninety-three weighed less than 1 oz. It need scarcely be stated that such a disintegration of the shell would be far too considerable to render the latter of value as a destructive missile, but the results showed that a small proportion in weight of this potassium picrate powder, if it could be used in

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shells, would suffice to produce the desired breaking up of the shell and violent scattering of the fragments, and that, therefore, the thickness of metal of the shell, and its consequent destructive power, might be very considerably increased. The chilled iron or Palliser shells, which, being of considerable thickness, hold comparatively small charges of powder, would obviously be rendered much more destructive, as shells, by substituting for the powder charges an explosive agent even considerably less violent in its action than the one just cited as an example.

In 1869, Designolle made at Bouchet three varieties of powder consisting of mixtures of potassium picrate and nitrate, with or without the addition of charcoal. Their compositions were as follows:

	Torpedo and Shell.		Cannon.			Musket.	
			Ordinary.		Large Calibres.		
Potassium picrate	55	50	16.4	9.6	9	28.6	22.9
" nitrate	45	50	74.4	79.7	80	65.0	69.4
Charcoal	....	....	9.2	10.7	11	6.4	7.7

These powders were made in the mill by ordinary gunpowder processes, from 6 to 14 percent of water being used and the trituration being 3 hours for torpedo powder, 9 hours for cannon, and 6 hours for musket. They were granulated as usual.

The torpedo and shell powder were tried at Brest and Toulon and gave excellent results. According to Roux and Sarrau, the heat of the combustion of the 55 percent mixture will be 916 cal. and of the 50 percent 1180 cal. and the temperature of combustion of the second powder will be equally increased. The cannon and musket powders

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were noticeable for their great uniformity of action, the variations in the initial velocities of the projectile being not more than 2 meters. According to Jouglet, 60 grams of Designolle powder produced the same result as 350 grams of ordinary powder, while the force of these mixtures could be varied between quite wide limits, according to the percent of picrate which they contained. In spite of their superior ballistic properties, Designolle's powders appear to be less brisant than black powder. Besides, they give scarcely any fumes while burning, and they do not erode the piece in which they are fired. Finally, the picrates constitute a series of crystalline bodies of definite composition and known reactions, and there is no reason to apprehend that "spontaneous" decomposition may take place with them, as it sometimes does with nitro-glycerine and the other nitric esters.

Ammonium picrate, $C_6H_2(NO_2)_3ONH_4$, is prepared by saturating warm picric acid with concentrated ammonia water. When neutralization is complete another charge of picric acid is dissolved in the same liquid and ammonia again added. This is repeated several times, and the liquid allowed to stand, when the salt crystallizes out in transparent orange colored prisms. It may also be obtained crystallized in beautiful citron-yellow needles by treating picric acid with ammonium carbonate.

According to Hill* and Abel†, if flame is applied to this salt it burns quietly with a strong smoky flame. If heated, it melts, sublimes and burns without any tendency to explosion. It is almost entirely unaffected by blows or friction. According to Desortiaux‡, it explodes when heated to about 310° C, but, if heated in free air to a temperature below 300° C, it fuses and burns with a

*Notes on Explosives, p. 50, Boston; 1875.

†The Recent History of Explosive Agents, p. 94.

‡Traité sur la Poudre 2, 740; 1878.

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beautiful fuliginous flame, and its explosion by a blow can be effected only with great difficulty.

Brugere in France and Abel in England simultaneously proposed powders formed of mixtures of ammonium picrate and potassium nitrate for use in firearms and, especially, in shells. These mixtures require very powerful blows to develop slight and partial explosion, and they exhibit no tendency to ignition when subjected to very severe friction.

Brugere's Powder (1869) is composed of

Ammonium picrate,	54
Potassium nitrate,	46

Heated to 310° C it burns with one-half the velocity of ordinary powder. Its force is not less than twice or three times that of black powder. It is only slightly hygroscopic, leaves but little residue, which consists of potassium carbonate only, and which is non-erosive; gives off but little fumes; and produces inodorous gases. The experiments made with the Chassepot showed that 2.6 grams of this powder produced the same effect as 5.5 grams of regulation powder. The equation adopted by Brugere to express the reaction is

$$C_6H_2(NO_2)_3ONH_4 + 2KNO_3 = 5CO_2 + 3N_2 + 3H_2 + K_2CO_3$$

and from this, 100 grams of the powder ought to give 69.14 grams of gaseous products which, at 0° and 76 cm., would have a volume of 52.05 liters. A direct determination gave 48 liters. If we compare this with the analogous results for black powder, as found by Bunsen and Schischkoff, we find the ratio of the volumes to be as 2.5:1. It, however, is not likely that a reaction which yields CO_2 and free H, at the same time, is likely to take place.

Brugere's powder is stable and comparatively safe to make and use, but it is rather costly.

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Abel's powder is a mixture of ammonium picrate and potassium nitrate and charcoal. When flame is applied to particles of the mixture, the individual particles deflagrate with a hissing sound like that of a sudden escape of steam, and the deflagration has little or no tendency to spread to contiguous particles; but, if the mixture be strongly confined, as in shells, it explodes violently, and exerts a destructive action, less formidable than that of gun-cotton, nitro-glycerine preparations, and potassium picrate powder, but considerably greater than that of gunpowder, and it was, therefore, considered likely to prove a valuable substitute for gunpowder when greater violence of action is desired with shells of small capacity. Shells charged with picric powder have been fired in England without a single casualty from guns of different calibres, ranging to the 9-inch gun, with the employment of a battering charge of 43 lbs. of R. L. G. powders. The safety of this substance was, therefore, sufficiently established to warrant the institution of thorough trials of its power as an explosive agent for shells. It is a curious and important circumstance connected with this mixture, that, though ammonium picrate and potassium nitrate undergo mutual decomposition, with the production of deliquescent ammonium nitrate, if the two be *dissolved* together in water, the addition of sufficient water even thoroughly to moisten the mixture appears to induce no such change, as the latter, when dried again, has no increased tendency to absorb moisture from the air, which it scarcely does to the same extent as gunpowder. The picric powder is, therefore, quite equal in permanence to gunpowder, and, as water may be used in incorporating the ingredients without any detriment to the stability of the mixture, its preparation is, at any rate, not more dangerous than the manufacture of gunpowder, and it

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may be safely submitted to the pressing and granulating processes which are applied to the latter.

Some comparative experiments have been instituted between picric powder and dry compressed gun-cotton in submarine mines, the results of which indicated that the two were not very widely different from each other in regard to their destructive action, when applied under the pressure of water most advantageous to the development of their explosive force. Although *wet* compressed gun-cotton is decidedly the more efficient agent of the two for use in submarine mines, the granular form of picric powder renders the latter susceptible of employment with decided advantage in small offensive torpedoes (such as the spar and Harvey) as they can be more conveniently and completely filled with the explosive material than with the disks or blocks of gun-cotton usually employed.

Abel's picric powder was made and tested at this Station by Professor Hill*. The mixture he used was composed of

Ammonium picrate,	42.18
Potassium nitrate,	53.97
Charcoal, best alder,	3.85

This was moistened with water, worked under the wheels, granulated, etc., as in the ordinary gunpowder processes. The powder obtained had a yellowish-green color, granulated well, and gave no difficulty in working.

On comparing this picric powder with gunpowder, by determining the amount of each necessary to burst cast iron spherical shell, the force of the picric powder was found to be to that of the gunpowder nearly as 1.75 to 1. The picric powder, however, seemed to burn imperfectly, giving off a heavy greenish-yellow smoke. This was due

*Rept. Secy. Navy, p. 173; 1876.

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partly to the fact that it was worked under the wheels but a short time; but it is also evident, from an examination of the proportions used, that the saltpetre was probably in insufficient quantity. A large number of experiments were made with this powder, as a charge for fuses and igniters, with good results.

Mr. S. H. Emmons claims to have prepared a new nitro-substitution product by dissolving an excess of commercial picric acid, by the aid of a gentle heat, in concentrated, fuming nitric acid (50° to 52° Baume'). The operation is effected without danger, as the mixture is refrigerating, though oxides of nitrogen are given off. On evaporation the solution deposits first, rhomboidal crystals of a fine yellow color, next, crystals of a paler yellow color, and lastly, a body having a light brown color. The three substances are said to be isomeric and to have a composition approximating to $C_8H_7(NO_2)_3O_2$. It is claimed that this body and the compounds which it forms with metallic radicals are explosive, but, in making Emmensite, this body, which is called "Emmens Acid," is mixed with both picric acid and a nitrate, preferably ammonium nitrate, and the whole fused together and cast in a mold. The result is a solid mass, of a bright yellow color, bitter taste, nearly inodorous and possessing a very porous structure.

EMMENSITE* is proposed for use both in industry and war, and for projecting as well as bursting charges. It is claimed to be insensitive to shocks, blows or fire, but more powerful than nitro-glycerine when detonated. When used in the granulated form for a projecting charge it is claimed to produce neither smoke, nor does it foul the piece.

Carbolic acid and picric acid are not the only bodies from which nitro-substitution compounds may be formed.

*Proc. Nav. Inst. 14, 435; 1888.

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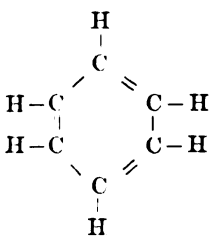
On the contrary, there are many such substances, and, notably, among these are the hydrocarbons, such as benzene, C_6H_6, and naphthalene, $C_{10}H_8$.

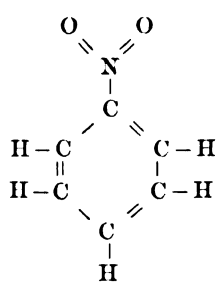
By acting upon benzene with strong nitric acid the mono-nitro-benzene, $C_6H_5NO_2$, is formed. This is a liquid and is characterized by possessing a powerful odor precisely like that emitted by the essential oil of bitter almonds. By acting upon the mono-nitro-benzene with strong nitric acid three different solid di-nitro-benzenes may be formed, viz., the ortho, meta and para, all being expressed by the same formula, $C_6H_4(NO_2)_2$.

In the same way by acting upon naphthalene with nitric acid or a mixture of nitric and sulphuric acids a great number of nitro-napthalenes can be formed, all of which, like the nitro-benzenes and tri-nitro-phenol, may be exploded by a detonator, and which are used as explosives, though generally when mixed with oxidizing agents.

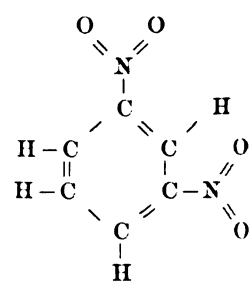
The manner in which the oxides of nitrogen are introduced by substitution into the molecules of benzene, phenol and naphthalene may be more readily understood by the use of structural formulas, thus,



Benzene.



Mono-nitro-benzene.



Meta-di-nitro-benzene.

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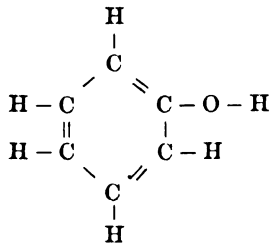
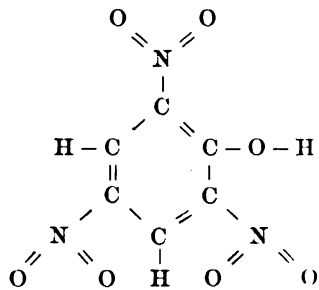
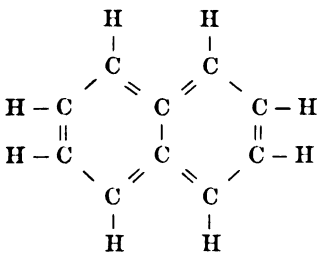


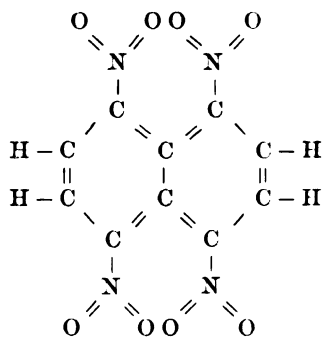
Phenol.



Tri-nitro-phenol or Picric Acid.



Naphthalene.



Tetra-nitro-naphthalene.

One of the best known of these mixtures is Rack-a-rock, 240,399 pounds of which was used in the blowing up of Flood Rock. This consists of potassium chlorate and mono-nitro-benzene (Sp. gr. 1.33) in the proportions of 79 parts of the first to 21 parts of the latter. These substances are transported and stored separately until wanted for use, when the mixing is effected either by pouring the liquid upon the solid or immersing the solid in the liquid. For this purpose the solid is supplied in the form of loosely packed cartridges of different sizes put up in bags closed at each end, and the combination of the ingredients is effected by means of a wire basket

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to receive the cartridges, which is suspended from a spring balance and dipped in a galvanized iron pail containing the fluid. A little attention to the time of immersion renders the absorption fairly uniform. The explosive is a compact solid having a specific gravity of about 1.7. According to Gen. Abbot, it decrepitates with difficulty when hammered on an anvil, but hardly ignites on wood. A fuse containg 24 grains of mercury fulminate fails to explode a cartridge which is unconfined or loosely confined. Even if compacted in an auger-hole in a log and tamped with mud, the explosion is only partial, but two such fuses determine an explosion of the first order. A cartridge struck by a bullet from a Springfield rifle flashes but does not detonate. Ordinary friction seems to have little tendency to cause explosion. The mean pressures obtained when fired under water was 108 percent of that of dynamite No. 1.

Mr. Divine, the inventor of rack-a-rock, has patented several other mixtures in which sulphur, "dead oil" of tar and carbon disulphide are mixed in various proportions with the potassium chlorate and nitro-benzene.

KINETITE is made by dissolving soluble gun-cotton in nitro-benzene and kneading potassium chlorate and nitrate, ammonium nitrate and similar compounds and a little antimony sulphide into the resulting jelly. High power, great stability and cheapness are claimed for this explosive, but the English Inspectors are not yet satisfied as regards its security in use and storage. This explosive was invented by Messrs. Petry, Fallenstein and Lisch of Duren, Germany.

BELLITE, discovered by Carl Lamm of Sweden, consists usually of ammonium nitrate and meta-dinitro-benzene which, when in a melted condition (the melting point is 80° to 90° C), are mixed with saltpetre. When pressed

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warm it has a specific gravity, in its granulated condition, of 1.2 to 1.4, and a gravimetric density of .8 to. 875.

Heated in an open vessel bellite loses its consistency at 90° C, but does not begin to separate before a temperature of 200° C is reached; at that point evaporation begins, and increases with a higher temperature, without, however, explosion occurring. If the heating is sudden, bellite will burn with a sooty flame, something like tar; but if the source of the heat is removed, the bellite will cease burning and assume a caramel-like structure, the ingredients being the same as in its original state, with the exception of a somewhat reduced proportion of saltpetre. The explosive appears to absorb very little moisture from the air after it has been pressed; if this operation is performed in the hot state, the subsequent increase of weight is only 2 per cent.

From the experiments of Werner Cronquist and Professor Cleve we learn that when bellite is subjected to the most powerful blow a man is capable of inflicting with a steel hammer upon an iron plate, it becomes heated, but neither explodes nor ignites. Two grains of bellite in a blank copper cartridge (that of a Remington rifle) were placed on an iron plate and subjected to the fall of a weight of 200 pounds from a height of 17 feet 6 inches, without exploding. Layers of bellite, .47 inch in thickness, on wood or iron have been pierced with rifle balls fired at a distance of some 50 yards, without showing signs of explosion or ignition. While boring in cast iron with a steel drill, one grain of bellite has been placed in the hole, neither explosion nor ignition having resulted, although no sort of oil or other lubricator was used. A small quantity was fixed to the pointed end of a steel rod, and the rod knocked so hard against quartz as to produce sparks, yet there was no explosion. A

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good sized piece of bellite was placed in an open tin box and covered with gunpowder, the latter was ignited, the explosion throwing the bellite several yards in the air, but it did not explode. In a piece of hard wood a hole was made of the size of a penholder, two grains of bellite were pressed hard into the hole and this closed with a wooden cork. The wood was thrown into a coke fire and consumed, but there was no explosion. A compressed bellite cartridge was placed close to a rocky wall, and some three inches from it a cartridge of nitrolite (nitro-glycerine, gun-cotton and nitrate of ammonia); the latter charge was made to explode by a Stubine percussion cap, and after the explosion the bellite cartridge was found to have been crushed, and the powder into which it was turned was fixed to the rock. The bellite had consequently not exploded. The list of these experiments might be considerably increased, but sufficient has been said to prove that bellite can withstand blows, fire, friction, and vibration, without the slightest risk of explosion. It can be safely transported by rail, and stored without any danger of spontaneous combustion.

Granulated bellite is caused to fully explode by the aid of a small quantity of fulminating mercury, even if its cover only consists of thin tin. When pressed warm, especially when it is in the form of hard cakes, it requires a stronger impulse and a stronger cover, which must adhere to the bellite.

The suitability of bellite as an explosive for grenades (when these are provided with a proper percussion tube) has been established through a series of experiments carried out by officers of the Swedish Royal Artillery. A series of experiments have been made by exploding mines loaded with bellite under water against a dynamometer. The average of several explosions gives, at a distance of

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17 ft. 6 in., a blow of equal power to that caused by a weight of 22 pounds falling from a height of 39 in. At a reduced distance of 12 ft. 6 in. the effect was proportionally increased. On comparing the efficiency of bellite with that of gun-cotton, under exactly similar circumstances, the former shows a superiority of 10.4 per cent. at a distance of 17 ft. 6 in., and of 15.2 per cent. at a distance of 12 ft. 6 in. The firing of 25-millimetre machine-gun ammunition and steel bullets against mines loaded with bellite had not the least effect upon the explosive, thus proving it to possess a great advantage in this respect over other explosives generally used for submarine mines.

It is the opinion of those who have had the best opportunities of judging, and whose verdict is of acknowledged authority, that bellite bids fair to become of great importance; that it is equally suitable for mining and military purposes, while it is not so liable to be put to an undesirable use as are most other powerful explosives.

SECURITE, in one of its varieties, according to Schœnweg, consists of a nitrated hydrocarbon mixed with an oxidizing agent, such as potassium chlorate, and with some organic salt which renders it flameless. The substance is not hygroscopic, is of a bright yellow color and can be kept without undergoing change. It cannot be exploded by a flame, nor by a hot body, but only by a detonating cap. Its power is said to equal that of dynamite No. 1, while it is much less costly.

In 1885, it was announced by the London *Times* that a new explosive, known as HELLHOFFITE, which had been invented by Hellhoff and Gruson, had been subjected at St. Petersburg to comparative trials with nitro-glycerine and ordinary gunpowder. The explosive is a solution of a nitrated organic compound (naphthalene, phenol, ben-

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zene, and the like), in fuming nitric acid. In preparing the hellhoffite tried in the experiments, dinitro-benzene, a solid, difficultly explosive, and badly burning body, was used. At the first trial glass bottles of 20 cubic centimetres each were filled with 20 grams of the respective explosive substances and corked. A primer of fulminate of mercury was passed through the cork, a slow match being attached to the outer end of the tube for the purpose of ignition. Each of the bottles thus prepared was placed on a truncated cone of lead, the upper diameter of which was 3.5 centimetres, its lower 4.5, and its height 6. The cone itself stood on a cast-iron plate 2.5 centimetres thick. The deformation of the leaden cone by the action of the explosives could consequently be taken as a measure of their respective destructive power. The explosion of the gunpowder, as was anticipated, caused no changes. By the explosion of the nitro-glycerine the cone was compressed about a quarter of its height; its surface had assumed the appearance of a well-worn hammer; the diameter of the surface had been increased to 5.5 centimetres. The explosion of the hellhoffite caused much greater changes. The surface of the cone was completely torn; pieces five centimetres long and two centimetres thick were torn off and thrown about for several paces; only half of the cone was still a compact but entirely defaced mass. At the second experiment bottles (of 25 grams each) filled with the various explosive substances were let into corresponding cavities bored into the face of fir blocks of similar dimensions. In exploding the gunpowder the block was torn into four pieces as if split with a hatchet, the several pieces were thrown about for 18, 12, 11, and 10 paces. In exploding the nitro-glycerine the block was split into several pieces. The upper portion of the block, as far as the bottle was let into it,

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was torn off transversely to the direction of the fibre in such a manner that a smooth cut was formed. The explosion of the hellhoffite likewise tore the portion of the block surrounding the bottle transversely to the direction of the fibre, and splintered the remainder of the block into a large number of thin fibres. The following experiments were also made with hellhoffite alone: A slow match was passed through the cork, as far as the surface of the hellhoffite in the glass bottle; no explosion followed on igniting the slow match. A quantity of hellhoffite poured into a bowl could not be exploded by a lighted match. Finally, a few drops of hellhoffite were poured on an anvil and exposed to heavy blows with a hammer, and no explosion followed. The hellhoffite, consequently, possesses the following advantages: (1) When detonated by fulminate of mercury it acts more powerfully than nitro-glycerine; (2) it may be stored and transported with perfect safety as regards concussion, as it cannot be exploded either by a blow or a shock, or by an open flame. On the other hand it has the following disadvantages: (1) it is a liquid; (2) the fuming nitric acid contained in it is so volatile that it can be stored only in perfectly closed vessels; (3) it is rendered completely inexplosive by being mixed with water, and consequently cannot be employed for works under water.

Capt. William H. Bixby, U. S. A., reported in 1886 to the War Department that during his visit to Magdeburg he had the opportunity of examining Gruson's new explosive of 1881,* which seems especially adapted to all military purposes wherever safe but violent explosive is required. This explosive, which is probably similar to that mentioned above, is described as being composed of two ingredients which can be transported with perfect

*Proc. Nav. Inst. 11, 771; 1885, and 12, 612; 1886.

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safety, are mixed only for use, and can be re-separated with ease at any subsequent moment, while it is more powerful than nitro-glycerine, safer than dynamite, produces no unpleasant effects upon those who handle it, and is cheap. In 1881–82 it was tried by the German Government, but, as usual, all results were kept secret. The composition of this explosive is still kept partially secret. One ingredient is strong nitric acid, and the other is a crystal; it is impossible to explode either alone, so that they are both perfectly safe as regards transportation. In order to make use of the explosive, the crystals are placed in the nitric acid, where they dissolve rapidly with a slight reduction of temperature; there is no chemical combination, but only a solution in this case; the mixture is then ready for use, but cannot be exploded by any ordinary method; for explosion it requires the use of a fulminating or detonating fuse twice as powerful as that used to explode dynamite. If, by any chance, after being thus prepared, the mixture is not required for immediate use, the addition of a little water dilutes the nitric acid to such an extent that the other ingredient is no longer held in solution; the crystals re-form, and can be separated by merely straining the mixture; the crystals are then dried (without the slightest danger), and are ready to be used again; the nitric acid is left in its diluted state and sold for other purposes. If the crystals are heated to a high degree of temperature, they burn, without explosion, somewhat like sealing-wax; neither ingredient alone, nor the mixture, can be frozen above zero Fahrenheit. Neither the crystals nor the mixture produce any other unpleasant effects on the persons who handle them except the usual effect produced by nitric acid. The nitric acid is strong, but not fuming, yellow in color, and very pure.

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The crystalline ingredient of this new explosive is Mr. Gruson's secret. It is a substance well known, to whose transportation there is no objection; it is, in fact, often transported to-day in commerce; it is not soluble in water, does not absorb water, and never becomes damp. Mr. Gruson discovered this explosive while experimenting to find some economical method for breaking up his old-iron chills. He thinks he has such facilities for its manufacture as will allow him to make it cheaper than other people.

This explosive has been tested by blows from a pile-driver, in order to see how liable it is to explode under percussion. A weight of 112 kilograms (246 pounds) falling one metre broke the case of the fuse without producing explosion; falling three metres, it still failed to produce explosion.

Two examples may be quoted to show the strength of the explosion: First, a chilled-iron cylinder of 30 inches diameter was torn all to pieces by the powder which filled an 0.8-inch hole along its axis. Second, one kilogram of the explosive was placed in a cast-iron shell of 75 pounds weight and exploded; the explosion tore the shell all to pieces in such a way that 240 of its fragments weighed in all only 37 pounds; the rest of the fragments were not to be found.

On the 29th of November, 1881, Capt. Bixby witnessed some experiments with this new explosive. The solid component looked like brown sugar, except that the crystals were needle-like, and nearly an eighth of an inch in length. When these crystals were placed in the flame of a Bunsen burner, they burnt slowly, in much the same way as sugar or sealing-wax, and with a good deal of smoke. Some of the crystals were put on an anvil and hammered without explosion. The crystals were then

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put into strong, but not fuming, nitric acid and were immediately dissolved. A few drops of the solution were put on the anvil and hammered without exploding. A piece of paper dipped in the solution was put in the flame of a Bunsen burner and it burnt in about the same way as the crystals had burned. A piece of paper put into the solution so as to serve as a wick was then ignited, and burnt with increased flame, but without igniting the solution. Water was then poured into the solution, and the solid component recrystallized into white, flaky crystals. This recrystallization was accompanied by a slight *reduction* in temperature, hardly sufficient to be noticeable to the touch. Some of the explosive mixture was then placed in a thin metal tube in the ground outside the building and exploded by the use of a friction primer of triple the strength ordinarily used for exploding dynamite; the explosion produced a very effective result. The brown crystals were said to be poisonous if eaten, but not poisonous to produce any bad effects if simply tasted or handled. An actual test showed that they were slightly astringent, with something of the taste of quinine. The strength of the explosive is estimated at 1.3 times that of nitro-glycerine, and its cost is 25 cents per pound.

About 1880, Hellhoff, of Berlin, patented a process for making explosives from crude coal-tar oils by direct nitration with strong nitric acid.* The mixture of various nitro-substances thus obtained was washed and dried, then mixed with oxidizing substances. The alkaline nitrates, chlorate of potash, and the strongest nitric acid served for this purpose. Experience gained by long-continued manufacture with the aid of steam proved that the separate fractions of the crude tar oils, even

*Deutsche Industrie-Zeitung, No. 36.

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those of the highest boiling point, were capable of nitration and gave satisfactory yield of nitro-derivates.

The question naturally arose whether the tar itself could not be nitrated and utilized for making explosives. Experiments made in this direction soon showed that the treatment of coal-tar with strong nitric acid was a very dangerous operation, that its employment on a large scale would be attended with great difficulties, and the greater part seemed to be burned up and lost. In subsequent experiments, therefore, an acid of 1.33 to 1.45 specific gravity was employed. The liquid tar was gradually stirred into the acid, the surface of the acid becoming covered with it. After a while this layer of tar contracted on stirring and settled slowly to the bottom. In about ten minutes the mass at the bottom puffed up, and gradually changed from a liquid to a solid or pasty state. The completion of the operation could be recognized by the mass rising from the bottom and spreading itself evenly over the surface. When the acid had all been used up, the tar which was added no longer contracted and settled to the bottom. The chemical changes did not produce an excessive amount of heat, so that cooling was unnecessary.

The product thus obtained was well washed with excess of water, and the sour wash-water that remained in its pores was expressed out. The purified product was then mixed with the oxidizing bodies above mentioned. One part by weight of the product dissolved very slowly, with the evolution of but little heat, in three parts of nitric acid, specific gravity 1.52. All these substances gave new explosive compounds of different degrees of violence. The power possessed by a solution of these new nitro-derivatives in concentrated nitric acid was shown by the fact that a small quantity of it, when ex-

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ploded by a double dynamite exploder, was able to shatter an iron shell.

Owing to the varying composition of the tar it is impossible to give the exact proportions in all cases of the oxidizing substances which must be added, but in the experiments it was found that two to five parts of concentrated nitric acid or chloric acid, or four to six parts of salts, were sufficient for one part of the nitro-derivative. The great advantages offered by this process are cheapness of material to be acted upon, the cheapness of the lighter acid used (the difference is about 60 per cent), and finally in the quiet and regular manner in which the operation takes place, permitting the use of simple and inexpensive apparatus.

These favorable results led to further experiments upon pitch, the paraffines and the mineral oils. The possibility of nitrating the latter seemed probable from their great similarity to the crude tar oils. Experiment, in fact, proved that they reacted exactly alike. But the strongest nitrating agents are required to act upon the purified mineral oils used for illumination. A mixture of equal weight of the strongest nitric and sulphuric acids, or a mixture of an alkaline nitrate with sulphuric acid, was employed.

On paraffines and similar products the weaker acids were as ineffectual as on purified oils. By the action of the nitrating agents mentioned upon purified mineral oils, nitro-compounds were precipitated, of a light yellow or light brown color, having the external appearance of rancid fat. These products were difficultly soluble in the strongest nitric acid. Pitch treated with nitric acid of 1.45 to 1.52 specific gravity gave a yellow-brown solution, and from this light yellow to brown scales separated on washing with water. The oil and pitch from wood-tar

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were treated with the weaker acid (1.45), and those from brown coal and stone-coal with the stronger acid (1.52). The products thus obtained were easily soluble in strong nitric acid with slight evolution of heat. These nitro-compounds when mixed with oxidizing bodies also formed powerful explosives, but the quantity of the latter required was two to four times greater than that added to nitro-derivatives of tar. There was found to be no special advantage in working these materials as compared with tar or even the tar oils, for a high grade of acid was required, while the increased quantity of oxidizing salts raised the price still higher. Still, this process is of some importance so far as pitch is concerned, since the price of tar is likely to increase as more uses are found for it.

All the special products of the distillation of coal having been found capable of being converted into explosives by nitration, it only remained to try an experiment on the original materials, coal and peat. Wood was excluded from the list, for its conversion into an explosive (pyroxline) had already been accomplished by Trauzl. It was found that the direct conversion of coal into an explosive by extracting the nitro-products would involve very expensive and tedious manipulations. After numerous unsuccessful experiments in which the product was either completely burned up or the coal was but slightly acted on, they tried gradual nitration. The coal, in form of a fine dust, was first treated with weak nitric acid, specific gravity 1.40 to 1.48; the weight of acid required was ten times that of the coal used. When stone-coal was introduced slowly into the acid the rise in temperature was inconsiderable, though some oxides of nitrogen were formed. The action was much more violent in the case of brown coal, and least so with wood coal. After the operation with any coal, a large portion of the material

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to be nitrated remained apparently unaffected and formed a thick sediment on the bottom of the vessel, while the nitro-product was dissolved in the acid layer above and imparted to it a light brown color—with brown coal nearly a tar color. When this fluid layer was well washed with water the nitro-product was thrown down as a fine brown powder. This precipitate was filtered out and washed repeatedly until the wash water was no longer acid. The sediment was also washed several times to remove the exhausted acid, then dried and finally treated with the most concentrated acid. It separated into two layers; the liquid one was treated just as before described to obtain the nitro-product suspended in it. Again the precipitate was brown, either light or dark. The solid residue was again washed and dried, then treated with the most powerful nitrating agents. In this way they succeeded in converting nearly all the brown coal and stone-coal into nitro-bodies, as well as the larger portion of the wood-coal. The yield was scarcely sufficient to compensate for the large consumption of acid, especially with the wood charcoal and coke. All the nitro-products obtained were nearly alike in color, state of aggregation, and other properties. They were insoluble in water, soluble in alcohol, and the most concentrated in nitric acid, and burned with strong aromatic odor, and were heavier than water.

The results of the experiments made on peat were considerably more encouraging, different kinds being tried. A firm, solid kind called "bog peat" (*Moortorf*), from Duneburg, was tried after a small test had shown that the reaction would not be too violent. It was first subjected to the action of equal parts, by weight, of the strongest nitric and sulphuric acids for several hours. The substance changed color from dark brown to dark

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red. Ignited in the air it burned with a lively flame and strong aromatic odor. When soaked in a solution of chlorate of potash and dried, it formed a powerful explosive. If the same peat was well pounded before the nitration, so that the humus substance was separated from vegetable fibres, and a larger surface was exposed to the powerful action of the acids, the earthy humus constituents were converted into a dark-brown, liquid, sticky nitro-body, having the external characters of that obtained by nitrating the heaviest tar oils. Its action when mixed with oxygenated bodies is also just like the latter. The other nitro-substance, formed from the finely divided fibres left in the dry distillation that attends the formation of peat, yielded an explosive without any admixture of an oxygen-bearing salt. In the open air it burnt very rapidly, leaving a slight carbonaceous residue.

Peat containing animal admixtures acts just like this bog peat. Peat that seemed to be of later formation would not bear the action of concentrated acids. There was a violent evolution of oxides of nitrogen, and in spite of the most careful cooling the heat became so great that there was danger of its reaching the ignition temperature of the nitro-derivative, so that the process had to be interrupted. The same peat was then mixed with ordinary commercial nitric acid, specific gravity 1.35, and as the action of this acid was scarcely perceptible, concentrated acid was gradually added until the process began to be quite violent. The acid had then been brought up to a gravity of 1.45. After the reaction had gone on for several hours with careful cooling, the product was washed and dried. This was an explosive without the admixture of the oxidizing body, but not so strong as that made from bog peat with the stronger acids. Others of the newly prepared nitro-derivatives, especially those

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from the crude tar oils by repeated nitrations, form explosives alone; but they are always weaker than when mixed with oxygenated bodies.

The manufacture of explosives from peat, owing to the cheapness of the material and its wide dissemination, as well as the simplicity of the process, is doubtless an important step in advance.

The chief characteristics of the newly-prepared nitro-substances are the following: The specific gravity of all is very nearly that of water. They all possess a powerful aromatic odor, resembling the fruit ethers, which is particularly noticeable on burning them. All solutions of these substances have a strong refractive power. The greater part of them are soluble in the strongest nitric acid, as well as in alcohol; they are all insoluble in water. In the open air they all burn with a bright, but more or less smoky flame. Their molecules are so unstable that they can be exploded alone, or, mixed with oxidizing substances, by simple ignition.

In 1873, Dr. Hermann Sprengel, in an extremely valuable paper in the *Journal* of the Chemical Society of London, proposed a new class of explosives which should be non-explosive during manufacture, storage and transport, but be powerfully explosive when prepared and detonated. His plan was to employ mixtures of combustible and oxidizing substances which should be kept separate until needed for use, but the novelty of the scheme was that these bodies should either all be liquids, or that part should be solid and part liquid, for, by taking advantage of the liquid state, speedy and intimate mixing could be realized and ensured. Among the oxidizing agents proposed were the nitrates and chlorates, which are solid, and nitric acid and nitrogen tetroxide, which are liquid. Among the combustible sub-

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stances were the nitro-substitution bodies, carbon disulphide, petroleum, and the like.

On glancing over the explosives preceding this it will be observed that many of them belong to the *Sprengel Class*; rack-a-rock, hellhoffite, and some forms of emmensite, being among the number, while roburite, which has recently received favorable mention, apparently also falls in this class.

Although not containing nitro-substitution compounds, panclastite and Parone's explosive may properly be spoken of here since they belong to the Sprengel class.

PANCLASTITE, invented by Eugene Turpin, consists of combustible substances, mixed with liquid nitrogen tetroxide. Carbon disulphide is preferred for this purpose, and the best proportions are two volumes of CS_2 to three volumes of N_2O_4.

PARONE'S EXPLOSIVE consists of two parts of potassium chlorate and one of carbon disulphide.

Reference books, *Proceedings U. S. Naval Institute, Hill's Notes on Explosives, Traité sur la Poudre by E. Desortiaux.*

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LECTURE VI.

FULMINATES.

In treating of the fulminates it seems proper to include in this group not only the salts of "fulminic acid" but also those substances which, like the fulminates, undergo, under normal circumstances, a detonating explosion only. We mean by this term *detonation* an explosion which requires but an exceedingly brief interval of time for its complete development, even when the mass of the explosive engaged is very large.

The simplest example (from a chemical standpoint) of a detonating substance is found in Nitrogen Chloride, which is one of the most unstable of explosive bodies. Although its explosive force, as calculated by Sarrau from the products of its decomposition, is but slightly greater than that of gunpowder, yet, as the reaction is a detonating one, the local application of the force is very marked and its effects very severe. Hence it is regarded as one of the most dangerous of explosive substances and one of the best examples of a detonating substance.

The name nitrogen chloride is usually given to the very explosive compound discovered by Dulong in 1812, which results from the action of chlorine on ammonium chloride. Its composition is somewhat uncertain, as its instability renders its analysis very difficult. Some chem-

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ists regard it as NCl_3 (trichloramide), that is ammonia in which all the hydrogen has been replaced by chlorine, while others hold that the compound contains hydrogen, the replacement of the hydrogen in the ammonia being incomplete. These views may be expressed by the following formulas:

H	H	Cl	Cl
H–N–H	H–N–Cl	H–N–Cl	Cl–N–Cl
Ammonia.	Mono-chlor-amide.	Di-chlor-amide.	Tri-chlor-amide.

Probably both views are right and that there are several of these chloramides.

It is obtained in the form of a yellow, heavy, oily liquid (Sp. Gr. 1.65) volatilizing easily and yielding a vapor of a very characteristic odor which affects the eyes. When heated to about 93° C it explodes with great violence, emitting a loud report and a flash of light. Its instability is, of course, attributable to the feeble attraction which holds its elements together, and the violence of the explosion, to the sudden expansion of a small volume of the liquid into a large volume of nitrogen, chlorine and, perhaps, hydrogen chloride. As might be expected, its explosion is at once brought about by contact with substances which have an attraction for chlorine such as phosphorus and arsenic; the oils cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently, whilst acids, having no action upon the chlorine, are not so liable to explode it. It has actually been distilled at 71° C, in air, without explosion.

Nitrogen chloride may be prepared by placing 3 grams of mercuric oxide in a bottle of 25 $\frac{^3}{cm}$ capacity filled with chlorine and adding 15 $\frac{^3}{cm}$ of water. The bottle is closed

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with a stopper and shaken, loosening the stopper occasionally, as long as chlorine is absorbed. The solution of hypochlorous acid thus obtained is filtered from the residual mercuric oxychloride and poured into a small clean beaker glass. A lump of ammonium chloride weighing 1.5 grams is then dropped in the solution, and the glass is placed under a stout wooden box. After the lapse of twenty minutes, the nitrogen chloride may be exploded by inserting, through a hole in the box, a stick dipped in turpentine, fixed at right angles to a longer stick. The glass will be shattered into very small fragments.

The substance may also be prepared by inverting a bottle of chlorine, perfectly free from greasy matter, over a leaden dish containing 1 part ammonium chloride in 12 parts of water. Drops of a yellow, oily-looking liquid will gradually collect on the surface of the solution and fall to the bottom, whilst the chlorine slowly disappears.

Also we can obtain it by placing a saturated solution of ammonium chloride in a funnel, the neck of which is cut off short and stopped with a cork through which two platinum electrodes are passed. A little turpentine is poured in so as to form a thin layer over the solution of ammonium chloride, and the electrodes are connected with a Bunsen battery of four or five cells. Bubbles of nitrogen chloride are thus formed, and are exploded as they rise to the surface and come in contact with the turpentine.

If we consider the trichloramide only, the reaction of its decomposition will be represented by the equation

$$2\,NCl_3 = N_2 + 3\,Cl_2,$$

hence one equivalent (120.5) in grams will furnish 44.64 liters of gas, or 1 kilogram will yield 370.5 liters.

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Although of no importance in practice, still, from its constitution and properties, nitrogen chloride is of great interest in the study of explosive substances. In the first place it differs from the other explosives which we have studied in the fact that though a markedly explosive compound, yet it does not contain any oxygen, and hence the explosion does not result from combustion having taken place. The fact that the products of the explosion are elementary substances goes to support this view. How then is the explosion brought about? This phenomenon has long been a matter of speculation, and no light has been thrown upon it until quite recently, when by the aid of thermo-chemical investigations a very reasonable explanation of it has been reached.

This science of thermo-chemistry has been developed during the last eighteen years, chiefly through the independent labors of Thomsen of Copenhagen, and Berthelot of Paris, and of their pupils, and, as its name indicates, it treats of the thermal phenomena which accompany chemical reactions. It is true that it was observed long ago that when bodies such as hydrogen and oxygen, or carbon and oxygen unite, heat is evolved, and measurements were made of the amount of heat evolved from unit masses of the substances, but no very extended study of these phenomena was made; and from the observations that were made the inference was drawn that all synthetical changes were attended with the development of heat, while all analytical changes were attended with the absorption of heat.

The study of thermo-chemistry has shown that this is by no means always true; that there are on the contrary many synthetical reactions which are attended with a marked absorption of heat, while the compounds resulting from these syntheses evolve heat when decom-

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posed. Hence chemical compounds have been classified, according to the thermal phenomena attending their formation, into two classes, viz., exothermous bodies and endothermous bodies; exothermous bodies being those whose formation is attended with the evolution of heat, and endothermous bodies being those whose formation is attended with the absorption of heat. It is obvious that all endothermous bodies must be more or less unstable, since, according to the principle of maximum work, they must constantly tend to break up into the simpler substances of which they consist.

Among the most remarkable of endothermous bodies is the nitrogen chloride, of which we have been speaking, for its decomposition is attended with the evolution of 38,100 gram-units of heat, and this explains its extreme instability and explosiveness. The remarkable fact thus brought into prominence might seem at first sight inconsistent with the general principle previously enunciated, that, while the union of atoms is attended with the development of heat, the parting of atoms involves a corresponding absorption. But it will be noticed on inspection of the reaction given above for the decomposition of trichloramide that the nitrogen atoms unite with each other to form molecules of nitrogen gas, and the chlorine atoms unite in a similar manner to form molecules of chlorine gas, and the amount of heat evolved by the union of these similar atoms so far exceeds the loss of heat which attends the separation of the dissimilar atoms of chlorine and nitrogen, that the difference amounts to over 38000 units.

All explosive compounds are likewise found to be endothermous either in relation to the elementary or simpler compound substances from which they are formed. So also all endothermous substances are unstable and

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many of them explosive, though not in the direct ratio of the heat which they absorb during formation. A notable example of this kind is acetylene, C_2H_2, whose molecules absorb nearly twice as much heat during formation as does a molecule of nitrogen chloride, but which is so stable that it cannot be exploded by heating, contact with flame or the electric spark, though it is detonated by mercury fulminate. These differences may, perhaps, be explained by differences in the arrangement of the atoms in the molecules.

Nitrogen Bromide or bromamide, whose composition is probably analogous to that of the chloride, may, according to Millon, be formed by decomposing nitrogen chloride with an aqueous solution of potassium bromide. It exists as a dense, blackish-red, very volatile oil, having an odor like the chloride, and explodes violently by contact with phosphorus and arsenic.

Nitrogen Iodide or iodoamide exists in the form of a brownish-black soft powder, which, when dry, explodes from the slightest cause, producing a loud report and destroying any solid bodies that may be near it. The explosion is attended with a faint flash of violet light, nitrogen being set free as gas, and iodine in the form of a very fine powder. It may be exploded by friction, even under water, and in the dry state can scarcely be touched without exploding, the slightest elevation of temperture, and even the friction produced by sliding over the surface of smooth paper being sufficient to explode it. When moist it decomposes slowly in contact with the air, yielding nitrogen, iodic and hydriodic acids. Under water in the presence of a beam of light it likewise undergoes decomposition, and this is so regular that Guyard has proposed to use it as a photometer, the amount of decomposition being measured by the volume of gas liberated.

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A similar decomposition is produced more rapidly by boiling water or alkaline solutions.

This body may be made by digesting iodine in excess of ammonia water; by adding a large excess of aqueous or alcoholic ammonia to a solution of iodine in alcohol, and then diluting with water; by adding ammonia to a solution of iodine in aqua-regia; or by decomposing nitrogen chloride with potassium iodide. The resulting black powder must be collected on a filter and washed with water; and, to guard against accidents in drying, it is advisable to divide the filter, with the moist precipitate upon it, into small pieces and expose them to warm dry air at considerable distances from each other; or the precipitate may be dried in a receiver filled with ammonia gas, in which case, according to Millon, there is no fear of an explosion.

Mallet makes this body by dissolving 30 or 20 grams of iodine in the least possible quantity of 95 percent alcohol and precipitating it by pouring it into a large volume of cold water. The finely divided iodine thus obtained is washed several times by decantation, then gently triturated for several minutes in a porcelain mortar with a large excess of the strongest ammonia water kept at or below 0° C, by a freezing mixture, the liquid poured off from the easily subsiding black powder, and replaced two or three times by fresh solution of ammonia. The powder is then transferred to a corked flask and shaken up repeatedly, first with alcohol of 95 percent, then with absolute alcohol, and finally with anhydrous ether, all of these liquids being artificially cooled. Most of the last portion of ether which, as well as several of the preceding washings, is perfectly coloress, is decanted off and the fluid black mud is turned out upon a filter, drained a few moments, and the remains of the ether swept away as

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vapor by placing the filter and contents under a receiver and drawing cold dry air through in a rapid stream. The product thus obtained is explosive in the highest degree, and in several instances has exploded in some quantity, through rubbing gently, under water, shattering the vessel in which it was held.

The composition of this body has been a much disputed matter. Colin and Gay-Lussac held that its formula was NI_3 that is that it was tri-iodoamide, while others found as the results of their analyses that it contained more or less hydrogen. In his research on the subject Mallet found that he could produce bodies in which the hydrogen of the ammonia was partially or wholly replaced, by varying the strength of the ammonia solution used, or the temperature and other conditions to which the substance was exposed. He, however, favors doubling the formula and on the following ground:

"In view of the general fact that the compounds of nitrogen in which this element behaves as a pentad are those in which instability is chiefly observable, and noticing the various proportions in which iodine and nitrogen have been found together united with it, it seems fairly probable that the molecule of each of these explosive compounds contains two pentad nitrogen atoms."

He finds the following compounds:

$$N_2I_6,\ NI_3.NHI_2,\ NH_2.NHI_2,\ \text{and}\ NHI_2.NH_2I.$$

Nitrogen Fluoride or fluoramide is produced, according to H. N. Warren, by passing an electric current through a concentrated solution of ammonium fluoride, and is deposited as oily drops on the negative plate. These explode with great violence on becoming connected with the positive pole, or with glass, silica or organic matter.

Silver Amine: Nearly one hundred years ago Berth-

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elot discovered that a powerful fulminating compound was produced by the action of ammonia upon silver oxide. This body has been recently examined by Raschig,* who has produced it by precipitating silver nitrate with sodium hydroxide and washing the silver oxide by decantation. Thus for each gram of silver nitrate used there was poured upon the silver oxide 2 $_{cm}^{s}$ of an ammonia solution containing 25 percent of NH_3. The oxide dissolved readily, leaving only a slight turbidity. The solution thus obtained was divided into several portions, each being placed in a dish about 10 cm. in diameter, so proportioned that no dish contained the oxide from more than one gram of the nitrate. Each dish was covered with a watch-glass and allowed to stand for 16 to 20 hours. The ammonia evaporated and the fulminating silver was deposited as a black, crystalline mass. After washing thoroughly it was analyzed, the results of some sixteen analyses leading to the formula Ag_3N. Samples prepared in other ways gave the same results.

This body explodes by the slightest concussion when dry and requires the greatest caution in handling even when moist. It is claimed to have been used as the initial detonating agent in the bomb that killed the Czar.† It has repeatedly been accidentally formed in the ammoniacal silver solutions used in the silvering of mirrors for astronomical purposes, and in the silver baths used in the wet process of photography, and has announced its presence by an explosion which in some instances has been quite disastrous in its effects.

A "Fulminating Gold" is formed as a buff precipitate by adding ammonia to a solution of auric chloride, or as a dark olive-brown precipitate by acting on auric oxide with ammonia. According to Raschig,‡ explosive com-

*Ann. der Chemie 233, 93-104; 1886.
†Proc. Nav. Inst. 1, 187; 1881.
‡Ann. der Chemie. 235, 341-368; 1886

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pounds result from the action of ammonia on either Au_2O, AuO, or Au_2O_3, though what has in the past been known as fulminating gold was produced from the Au_2O_3 or its chloride. According to Dumas' analysis, this body is a hydrated molecular compound of the gold oxide and ammonia, but Raschig's results show that this, as well as the compounds formed from the other oxides, are gold amines or gold ammonium compounds. All are explosive, the most violently explosive being the sesquiauroamine $Au_3N_2 + 6\,H_2O$.

Cupricamine, Cu_6N_2, is formed by passing a current of dry gaseous ammonia over finely powdered cupric oxide heated to 250° C; water and nitrogen gas are evolved, and the nitride is left as a dark-green powder, which, when heated to about 310° C explodes feebly, emitting a red light; strong acids decompose it with the evolution of nitrogen.

Mercury amine, according to Plantamour, may be made by passing dry gaseous ammonia over the dry yellow mercuric oxide, which is precipitated from mercuric salts by an alkali, so long as the gas is absorbed, and then heating the resulting black-brown mass, cautiously, at a temperature not exceeding 150° C, so long as water is given off. An anhydrous brown powder is produced, which detonates powerfully when heated or struck, and which is decomposed by acids into salts of ammonium and mercury. Miller considers it as being probably identical with a compound obtained by Weyl through the long-continued heating of the compound N_2Hg_4O in ammonia gas.

Fulminating Platinum is produced as an insoluble black powder by dissolving ammonium platinic chloride in a solution of sodium hydroxide and adding an excess of acetic acid, or by precipitating platinic sulphate with an

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excess of ammonia. This compound detonates violently when suddenly heated to 200° C, but is decomposed by acids with formation of ammonical salts.

Nitrogen Sulphide; This body exists in the form of beautiful golden-yellow rhombic crystals of Sp. Gr. 2.22. It detonates powerfully under percussion, but is less sensitive than diazo-benzene nitrate or mercury fulminate. It deflagrates at 207° C*, but more slowly than mercury fulminate. It is not affected by dry or moist air and has been several times heated to 50° C without change. It has a faint odor, adheres strongly to paper upon which it is rubbed, and irritates the mucous membrane of the nose and eyes most painfully. It is an endothermous substance, and when decomposed, according to the reaction,

$$2NS = N_2 + S_2,$$

it evolves 31900 units of heat. One equivalent in grams (46) gives 11.6 liters of nitrogen gas, or one kilogram yields 242.6 liters, but as at the temperature of the explosion (which has been estimated at 4375° C) the sulphur will also be gaseous, the total volume for one kilogram will be $485.2\ (1 + \alpha t)$ liters. The pressures developed by the explosion of nitrogen sulphide are very nearly the same as those of mercury fulminate for the same density of loading, but, owing to successive transformations of the sulphur vapor during cooling, the effects produced by this body when used for detonators and fuses ought to be very different from that of mercury fulminate.

The compound may be obtained by passing dry ammonia gas through a solution of sulphur dichloride in 10 or 12 times its volume of carbon bisulphide. The passage of the gas is continued until the brown color of the precipitate first formed disappears; the yellow liquid is filtered

*Berthelot, Miller gives 157°, and Watts 150°–160°.

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from the ammonium chloride which is produced, and allowed to evaporate spontaneously, when the nitrogen sulphide crystals are formed mixed with sulphur. The latter is dissolved out by carbon bisulphide.

The nitro-substitution compounds are believed to owe their explosive properties to the fact that they contain nitrogen which exists wholly or in part in the body, united with oxygen, in the form of nitryl NO_2. In 1860 Griess discovered another class of nitrogenized bodies, some of which are explosive, which may be regarded as formed by the replacement of two atoms of hydrogen (in two molecules of an aromatic hydrocarbon) by two atoms of nitrogen. A body so constituted is called an *azo* compound. Diazobenzene $C_6H_5 - N \equiv N - OH$, which may be formed by the indirect substitution of hydrogen by nitrogen in benzene, is a type of this class. Diazobenzene is a quite unstable substance, while the nitrate is a crystalline solid, which is employed in the arts for the manufacture of dye-stuffs, and which is so explosive that it has been proposed for use as a detonating primer. It may be formed by the action of nitrous acid on phenyl-ammonium nitrate according to the reaction,

$$C_6H_5.NH_2.NO_3H + HNO_2 = C_6H_5.N_2.NO_3 + 2\,H_2O.$$

Berthelot and Vieille have made a study of the properties of diazobenzene nitrate,* and they consider it as representing the residue of two nitrogenized bodies which have lost, the one (nitrous acid) its oxygen, the other (aniline) a part of its hydrogen, in the act of combination; but a notable portion of the energy of these elements remains in the residue, which accounts for its explosive character. They have examined this substance

*Annales de Chemie et de Physique [5] 27, 194; 1882.

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in the same way as they have done for fulminating mercury.* If preserved in dry air out of contact with the light it can be kept for two months and more, but exposed to daylight it slowly changes; in moist air the the change is rapid, and in contact with water it is decomposed immediately. It is as sensitive to a blow as mercuric fulminate. On heating, it detonates with extreme violence at about 90° C, while mercuric fulminate detonates at about 187° C. Slowly heated at a lower temperature it slowly decomposes. Its density is 1.37. Total heat of combustion under constant volume + 783.9 cal. and under constant pressure + 782.9 cal. Heat of formation — 89 cal. showing it to be an endothermic † substance like the other high explosives.

The pressures found for diazobenzene nitrate are greater than those for mercury fulminate for the same density of loading, but on the other hand mercuric fulminate will develop a much greater pressure (24,000 kilos instead of 7200 kilos) when detonated in its own volume, on account of its greater density. The destructive effects of the two explosives differ, following the density of charge. On contact the effect is much more marked with mercuric fulminate.

Mercury Fulminate: Our knowledge of the substances which are chemically known as fulminates began in 1800, when Howard, an English chemist, discovered‡ mercury fulminate. The discovery was made while acting on mercuric oxide with alcohol and nitric acid in order to prove whether or not "hydrogen was the basis of muriatic acid," and the action resulted in the production of a whitish salt which crystallized in acicular needles possessing a saline taste and which, when dried, exploded with

*Proc. Nav. Inst. 8, 441.
†Proc. Nav. Inst. 8, 305.
‡Phil. Trans. 90, 204; 1800.

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extreme violence when a drop of sulphuric acid was poured upon them. Howard followed up his discovery and studied the properties of the substances as thoroughly as his facilities would permit, and he showed by his experiments that, while the body exploded with such extreme violence as to deeply bruise the metallic surfaces with which it was in contact, and that while it produced but little smoke, yet, as compared with gunpowder, it possessed but little power as a projecting agent, and, further, that when used as a substitute for a gunpowder charge in a gun, though it imparted only a low velocity to the bullet it burst the gun. Hence, although, from the comparative readiness with which the salt could be produced and the great power it manifested, high hopes were excited as to its uses as a substitute for gunpowder, these hopes were dashed to the ground by the extreme difficulty met with in controlling its violent action, and it found no practical applications until used for percussion caps and primers. Its most important present use as an agent for exciting the explosion of the high explosives, and for causing them to develop their greatest force, dates from 1863, when Nobel discovered that by the explosion of a few grains of this substance in the midst of a mass of nitro-glycerine, the nitroglycerine would be detonated, and this has since been found to be the case with all the other high explosives.

Investigation of mercury fulminate by Liebig, Gay Lussac and others has shown it to be a salt of an organic acid having the probable formula of $C_2N_2O_2H_2$, and which is known as fulminic acid. Although a large number of fulminates have been obtained the acid itself has not been isolated until recently, H. N. Warren* having now claimed to have effected this.

*Chem. News 57, 255; 1888.

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Quite a number of methods have been proposed and used for the manufacture of mercury fulminate, but the following has given us the most satisfactory results and is now in use at this station:

Ten parts by weight of mercury are dissolved by gentle heat in 120 parts of nitric acid (Sp. Gr. 1.4). When the solution is complete, the liquid is cooled and shaken to secure homogenity, and it is then poured into a glass flask containing 110 parts of alcohol (95 percent). The flask should have six times the volume of the alcohol. At an atmospheric temperature of 60° F, or above, action soons begins in this mixture, without previous heating, and is eventually quite turbulent. Dense white fumes are given off and, later, red fumes. It has been the practice in the past to add more alcohol at this stage, in order to moderate the violence of the action, from the fear that an explosion might ensue, but I have found that this addition gives rise, by reduction, to the formation of metallic mercury and compounds of mercury other than the fulminate, which seriously diminish the value of the fulminate as a detonating agent, while, on the other hand if the action is allowed to proceed without interruption, it never, or at least has never resulted in an explosion or anything approaching one, but it gradually exhausts itself, and the fulminate is left behind as a gray crystalline powder. If, when manufacturing, the temperature of the atmosphere falls below 60° F, it generally suffices to plunge the flask containing the alcohol and mercuric nitrate into warm water until the effervesence begins in the mixture, and then to remove the flask and place it in the open. When once the action begins, it will generally continue until the reaction is completed. Sometimes, however, the atmospheric temperature has been too low even for that, and in such

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cases I have wrapped the flasks in heavy felt, placed them in tin boxes and saturated the felt with hot water.

In any case the operation should always be conducted under a good draught and out of the presence of naked lights, or other sources of ignition, for the dense white fumes evolved contain mercury or mercurial compounds, which are poisonous when inhaled, and also ethyl nitrite, which is highly inflammable and which forms an explosive mixture with the air. The reactions attending the formation may, perhaps, be represented as follows:

(1) $HNO_3 + 3Hg = 3Hg(NO_3)_2 + N_2O_2 + 4H_2O.$

(2) $2HNO_3 + 2N_2O_2 = 2HNO_2 + 2N_2O_3.$

(3) $C_2H_5OH + HNO_2 = C_2H_5ONO + H_2O.$

(4) $C_2H_5ONO + HNO_2 = H_2C_2N_2O_2 + 2H_2O.$

(5) $H_2C_2N_2O_2 + Hg(NO_3)_2 = HgC_2N_2O_2 + 2HNO_3$

From these equations we should theoretically obtain 14.2 parts of mercury fulminate from every 10 parts of mercury used, but the best practice has not yielded more than 11.8 to 12.4. If the operation has been conducted as described the fulminate will be found as a pasty mass of fine gray crystals of a perfectly uniform color, and, as near as may be, uniform size. If solids of different colors are observed, or if globules of metallic mercury are seen, the operation has not been properly carried out and the charge is unfit for service use.

When the action has ceased in the flask we find that that the flask is so warm that it can barely be touched by the hand. It is now allowed to cool, and then it is filled with well filtered water, shaken, allowed to stand until the fulminate has fallen to the bottom, and then the clear supernatant liquid is decanted, and this operation is repeated until the decanted wash water fails to

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give the least acid reaction to litmus paper. Then the fulminate is transferred to a stone-ware or glass vessel where it is kept well moistened with water until desired for use. During the washing *extreme care* should be taken that no fulminate accumulates on the dishes or floor, or is carried into the drains, for serious accidents have resulted in factories from small quantities having been spilled and remained unnoticed until they have dried and then been exploded by a person treading on them. Should any be spilled it should be destroyed by means of a solution of an alkaline sulphide.

Mercury fulminate, as thus obtained, is in the form of fine crystals which appear under the microscope to consist of orthorhombic crystals which are twinned at right angles along the vertical axis. It is found by experience that the finer crystals are better for use in detonators than the coarser ones.

Dry, mercury fulminate explodes violently when struck or compressed, or rubbed between hard surfaces, when heated to 186° C, when touched with strong sulphuric or nitric acids, when in contact with sparks from flint and steel or the electric spark. When wet with thirty percent of water it is inexplosive, that is its explosion cannot be induced by any of the above-mentioned means, but I have recently proven that it may be completely and readily detonated, even when completely saturated with and immersed in water, by the detonation of a small amount of dry fulminate in contact with it. Though Abel has been able, under carefully contrived conditions, to cause mercury fulminate to undergo a gradual combustion, yet, in practice, dry fulminate, even when unconfined and even when in vacuuo, detonates.

The density of mercury fulminate is 4.42. Its heat of formation* (for one equivalent 284 grams) is — 62900

*Berthelot and Vieille, *Proc. Nav. Inst.* 8, *439;* 1888.

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calories. Its heat of combustion, in an inert atmosphere, is + 116000 cal. for constant volume and + 114500 for constant pressure. This quantity of heat would be sufficient to raise the temperature to 4200° C. Its heat of combustion in air is + 250900 cal. The reaction attending its decomposition may be represented by

$$HgC_2N_2O_2 = Hg + 2CO + N_2,$$

and from this equation we find that 1 gram of fulminate should yield 235.8 $\frac{c}{cm}$ of gas. From five determinations, Berthelot and Vieille obtained 234.2 $\frac{c}{cm}$. Therefore one equivalent (284 grams) furnishes 66.7 liters of gas at 0° C and 76 cm.

From the above equation it is seen that mercury fulminate does not give rise to the formation of any substance capable of undergoing a notable dissociation under the conditions of the experiment, consequently no gradual recombination can take place during the cooling which would retard the expansion of the gas and diminish the violence of the initial blow. This explains the brusqueness of the explosion. It would be still more brusque but for the condensation of the mercury vapor. In all cases the nature of the product explains the character of the explosive blow.

When mercury fulminate is mixed with potassium nitrate or potassium chlorate and exploded, the following reactions may take place:

$$5HgC_2N_2O_2 + 4KNO_3 = 3Hg + 8CO_2 + 7N_2 + 2K_2CO_3,$$

$$3HgC_2N_2O_2 + 2KClO_3 = 3Hg + 6CO_2 + 3N_2 + 2KCl,$$

the first of which evolves + 227400 cal., and the second + 258200 cal., the heat evolved here being double that from the pure fulminate, but the initial blow is tempered here by the phenomena of dissociation, due to the carbon

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dioxide, which render these explosive mixtures less brusque in their effects. The temperature is also reduced at the outset by the distribution of the heat among the more considerable mass of products.

The superiority of the power of mercury fulminate is manifested best when in contact with a body, and it is due to three causes: the nearly instantaneous decomposition of the body by simple inflammation; the almost total absence of dissociation products, and, finally, the great density of the explosive. By reason of these conditions, the definite products of the reaction appear to form all at once, before the matter has time to take a volume notably superior to that of the primitive solid. If, then, the fulminate detonates in a receptacle, in contact with the sides of the same, it developes on it, at the start, an instantaneous pressure which bears no definite relation to the mean pressure controlled by the capacity of the receptacle. Berthelot and Vieille have sought to estimate the pressures developed under these conditions of contact, and they find that the curve for the explosive substances, representing the tension in a closed vessel, tends rapidly toward an asymptote. Admitting this, mercury fulminate with an absolute density of 4.42 will develop in contact a pressure of 48000 atmospheres, whilst compressed gun-cotton, with a density of 1.1, such as is employed for military purposes, will develop in contact only 24000 atmospheres. Calculation will show that no other explosive known will give in contact an instantaneous pressure at all comparable to that of the fulminate. Without insisting too strongly on these numbers, it appears useful to notice them since they mark the general relations of these phenomena. The superiority of the effects produced by the explosive shock of the fulminate over that of other explosives is explained by this

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circumstance joined with the absence of dissociation; nothing can resist direct contact with this explosive.

In one Berthelot and Vieille's experiments the fulminate was deposited on the bottom of the steel calorimeter used, and while the mean pressure, calculated in advance, could not have been more than 50 atmospheres, yet the steel vessel was bruised all over the surface occupied by the charge, the contours of which were found impressed on the metal.

We know that fulminate of mercury is eminently fitted for determining the nearly instantaneous propagation of detonation, (which is so distinct from inflammation, properly called), aud which is indispensable for causing dynamite and compressed gun-cotton to develop their entire power. Berthelot has given elsewhere* a general theory in explanation of these characteristic effects, which refers the violence of the initial blow to the brusqueness of the successive decompositions, and also to the enormous pressure exerted at the point of contact during the course of these decompositions. These results sustain this theory and show why the fulminate of mercury is particularly adapted to provoke true detonations in other explosive bodies.

Mercury fulminate is largely used for filling percussion caps. For this purpose 100 parts of the dry fulminate are rubbed to powder with 30 parts of water, 50 to 62.5 parts of saltpetre and 29 of sulphur, the rubbing being effected by means of a wooden pestle on a marble slab. This mixture is dried sufficiently to admit of being granulated, after which it is forced, by means of machinery, into the copper caps, and simultaneously covered with either a layer of varnish or tin-foil, to protect from damp. The best varnish for the purpose is a solution of gum

*Sur la force de la poudre, 2d edit. 1872, 165.

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mastic in oil of turpentine. The caps are finally dried by a gentle heat, and packed in boxes. One kilogram of mercury converted into fulminate suffices for the filling of 40,000 gun-caps of the larger or military size, and for 57,600 caps of the size used by sportsmen.

Its use in the torpedo service is confined to the filling of detonators. The U. S. Navy detonator consists of a copper case made in two parts. The lower part is a No. 36 metallic cartridge case and is $1\frac{1}{8}$ inches long and $\frac{11}{32}$ inches in diameter. The upper part is a copper tube, $\frac{5}{8}$ inches long and $\frac{12}{32}$ inches in diameter, open at both ends, which has been cut from a No. 38 metallic cartridge case. A $\frac{3}{16}$-inch thread is cut on each of these parts so that the upper part or cap screws nicely on to the lower part. The lower part is filled with fulminate of mercury up to the lowest thread of the screw. The top part is fitted with a plug made of sulphur and glass, through which the detonator legs pass to connect the bridge with the wires leading to the battery. When the fulminate is dry the spaces in the lower case and the cap are filled with pulverulent dry gun-cotton, and then the parts are screwed together.

The making of the plugs, bridges and other parts, and the priming, closing, painting and packing of the detonators is carried on at the fuse room. The making of the fulminate and the charging, drying and testing of the charged cases are carried on at the laboratory under the supervision of the Chemist. For this purpose the cases are supplied in wooden blocks which hold them vertically. They are first carefully washed in gasoline, to free them from the oil and grease with which they become covered during the cutting of the threads, and then well dried.

A portion of the wet fulminate is then placed upon a

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linen filter and, when most of the water is drained off, the filter and contents are squeezed dry; the alcohol is poured over the fulminate in successive small portions until the last traces of water are removed. A portion of this fulminate is placed in a glass funnel with a graduated glass stem, the mouth of the stem is closed by the finger, and with a copper rammer the fulminate is forced into the stem until it reaches the mark for 35 grains. Then the finger is removed, a case slipped over the stem, and the fulminate is forced into the case and rammed tightly home with a copper or wooden rammer having a shoulder, which allows the top of the fulminate to be forced just to the bottom of the screw-thread. The charged cases are then replaced in the blocks and placed on shelves in a dry magazine to dry. Until recently the detonators were charged with fulminate wet with water and required three months to dry; by the present method we can dry them thoroughly in one week, and in a warm, dry, well ventilated room, in two days. This drying is of the utmost importance. When dry, the chemist tests them by firing ten percent of them in gun-cotton or on iron plates, and if *no* failures occur the remainder are sent to the officer in charge of the fuse room.

Other forms of detonators, known as blasting caps, will be found for use in the arts. They are of two forms and of several grades. They consist of thin copper cases about $1\frac{1}{8}$ inches long and $\frac{1}{4}$ inch in diameter. In one form they are open at the mouth, and these are for use with the Bickford or similar time fuses which are to be lighted by a match. For this purpose a piece of fuse of the desired length is inserted in the mouth of the cap so that the fuse composition touches the fulminate, and then with suitable pinchers or crimpers the mouth of the cap is *tightly* closed around the fuze. In the other form

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the mouth is closed with a wooden plug, sealed with sulphur and glass, which carries the legs connecting the bridge with the leading wires. This form is fired by electricity.

The different grades are known as single, double, triple, quadruple and quintuple force caps. The single force caps contain three grains of the fulminate, the others increase by three, so that the quintuple contains fifteen grains. The fulminate usually consists of 75 parts of mercuric fulminate and 25 parts of potassium chlorate, and it is pressed into the cap under a pretty high pressure. Sometime a little gum, dissolved in alcohol, is added to make the mass more coherent. The object of using the chlorate is to cheapen the cost and to render them more certain in firing low grade powders containing a gunpowder dope. The presence of chlorates, nitrates, sulphur, and the like, give rise to flame and incandescent particles, whereas mercury fulminate *per se* does not produce either.

Blasting caps are tested by firing the cap in a cork so placed that the base of the cap is flush with the bottom of the cork. The whole is then placed on a sheet of Swedish iron, which is supported on blocks placed under each of its four corners, and the cap is fired. A good cap should blow a clean hole through No. 14, A. W. G., iron.

Silver Fulminate: Silver fulminate has a composition similar to that of mercury fulminate, except that the acid hydrogen is replaced by silver instead of mercury. Its composition may be represented by the formulas $Ag_2C_2N_2O_2$.

According to Gay-Lussac and Liebig it may be prepared by dissolving one part of silver in 20 parts of nitric acid (1.308) and pouring this into 27 parts of alcohol of 87 percent. The mixture is heated to the boiling point,

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and, when it becomes turbid, it is removed from the heater and mixed with another 27 parts of alcohol to moderate the action. After the liquid is completely cooled about one part of silver fulminate is obtained.

The preparation of this substance requires the greatest caution. Capacious vessels must be used, so that the liquid may not boil over, as in that case the salt might dry on the outside and then explode. All flame must be removed to a distance lest the vapors should take fire. The mixture must be stirred with wooden rods and not with glass rods or other hard bodies. Contact with hard bodies should especially be avoided after the preparation is dry. Paper shovels must be used to transfer it, and it must be kept in vessels of paper or pasteboard, not of glass, as an explosion might arise from the friction of the glass stoppers. The vessels holding it must be loosely covered, as an explosion might arise from pressing the cover of the box on to fit it.

Silver fulminate forms small, white, opaque, shining needles, having a strong bitterish metallic taste, and is very poisonous. It is but slightly soluble in cold water, but dissolves in 36 parts of boiling water and separates on cooling. It dissolves much more freely in aqueous ammonia, and is left behind unaltered as the ammonia evaporates. When exposed to white or blue light it gradually blackens, giving off carbon dioxide and nitrogen, and leaving a black substance mixed with a small quantity of the undecomposed salt. It explodes much more violently than mercury fulminate by heat, by the electric spark, by friction or percussion, or by contact with oil of vitrol. A temperature of 130° C is sufficient to explode the dry fulminate. In the moist state it requires a much harder blow to explode it than when dry, but it will sometimes explode, even under water,

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by friction with a glass rod. It explodes with peculiar readiness when rubbed with glass-dust or sharp sand, and also, when dry, with the edge of a card. It may, however, be rubbed to powder in a porcelain mortar with a cork or with the finger. When well washed, and then exposed to the sun until dry, it explodes on the slightest touch. According to Schmidt, oil of vitrol causes moist silver fulminate to detonate as strongly as the dry substance. If unconfined gunpowder be mixed with silver fulminate, the gunpowder is not ignited by the explosion of the latter, but merely scattered about. When silver fulminate is thrown into an open bottle filled with chlorine gas, it explodes before reaching the bottom, and therefore the bottle is not burst. It is used for making crackers and detonating toys.

Besides those mentioned, a large number of other salts of fulminic acid are known, all of which are unstable and explosive.

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LECTURE VII.

GUN-COTTON.

Gun-cotton is, as its name implies, an explosive made from cotton. It is only necessary to immerse pure dry cotton in a mixture of the purest and strongest nitric and sulphuric acids to convert the cotton into gun-cotton. The purification of the cotton, the conversion of the cotton into gun-cotton, and the purification of the gun-cotton are all somewhat difficult of attainment, and hence the manufacture involves some lengthy and rather complicated processes. The necessity for these processes and their rationale can best be shown by reviewing the history of gun-cotton, for, in common with most of our modern processes, the present degree of attainment has been reached only through the labors and studies, the failures and successes of many investigators.

In 1832 Bracconot discovered that when starch, ligneous fibre and analogous substances were treated with concentrated nitric acid, a highly combustible body, which he termed *xlyoidine*, resulted. Pelouze repeated these experiments in 1838 and extended his investigations to cotton and paper, which he held were best adapted for the production of this substance. He found that the body could be inflamed at 180° C, either by a blow or by a strong pressure, and he recommended its use in pyro-

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techny. Later, Dumas prepared from paper, by this means, a substance which he called *nitramidine*, and which he proposed for use in making cartridges.

The products thus obtained were, however, found to be irregular in composition and unstable, and so no practical result flowed from these researches, until late in 1845, when Schœnbein of Basle announced the discovery of an explosive, which he called gun-cotton, and which he claimed could be used for all the purposes for which gunpowder was used, while it was four times as powerful as the latter. He kept his method of manufacture secret, but in August, 1846, Bœttger of Frankfort proclaimed his ability to make gun-cotton, and on conferring together it was found that the methods employed were the same, and hence the two formed a partnership for disposing of their secret to the German government, and the method remained unpublished.

However, on October 5, 1846, Otto of Brunswick gave, in the *Augsburger Allgemeine Zeitung*, a description of a process for making a gun-cotton which closely resembled that of Schœnbein's, and which consisted in plunging purified cotton into very concentrated nitric acid for about one-half minute and then washing and drying with great care, while nearly at the same time (1847) W. Knop of Hanover and Taylor of England discovered that gun-cotton could be prepared by using mixtures of nitric and sulphuric acids. These discoveries forced Schœnbein and Bœttger to reveal their secret and it was found that they too were using the mixed acids, the strength and proportions being as follows:

	Sp. Gr.	Parts by Weight.	Parts by Volume.
Nitric acid,	1.45 to 1.50	1	1
Sulphuric acid,	1.85	3	2.3

The acids were mixed in a porcelain or glass vessel

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cooled to 10° or 15° C. Then the cotton was plunged in, the proportions being one part of cotton to from twenty to thirty of the acid. After about one hour the cotton was removed, washed in a large quantity of water, then in a solution of potash to remove the last traces of acid, and, finally, with pure water to remove the salts which had been formed. The material was then wrung out, impregnated with a weak solution of saltpetre, again wrung out, and finally dried at a temperature of 65° C.

Taylor's process differed only in using one part of cotton to fourteen of the mixed acids. Heeren and Karmarsch used one part of fuming nitric acid to two of English sulphuric acid, while Knop used equal volumes of the two acids. Both of these latter allowed the cotton to remain but from four to five minutes in the acid.

From this time, experiments were undertaken in the United States, Germany, France, England and Russia, to test the value of this explosive as a substitute for gunpowder in guns, but the material was found to be quite unstable and gave rise to several terrible, and at the time, inexplicable explosions at Vincennes, Bouchet and Faversham, (1847–48), which, combined with the grave political disturbances of the time, led to the discontinuance of the experiments, except in Austria, where Baron Von Lenk was engaged in its study.

From a consideration of all the attending circumstances he concluded that the accidents above noted were due either to the failure to purify the cotton perfectly; or to the use of too weak acids, or too short an immersion, so that the conversion was incomplete; or to the failure to remove the acids completely from the gun-cotton.

The impurities which are present in cotton are of two kinds, natural and artificial. The natural consist of incrusting matter and oily matters. The artificial of oil

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and dirt generally, and water. When impure cotton is immersed in the acid mixture, the incrusting substance and greasy matters are acted upon by the acids and form compounds which are quite unstable, and which, if present in the gun-cotton, may give rise to decomposition in the gun-cotton itself. The moisture present serves both to dilute the acid mixture and to cause local heating during immersion, which causes waste of material and may give rise to the formation of unstable compounds which, if present in the gun-cotton, may also provoke spontaneous decomposition.

The use of weak acids or too short an immersion prevents the complete conversion of the cotton into the stable military gun-cotton. All chemical reactions require a certain time for their completion, and this is especially the case when the physical structure of either of the reacting bodies is such as to prevent rapid contact between them. The physical structure of cotton is such as to notably prevent the acids from rapidly coming in contact with all its parts, for it consists of long, flat, twisted tubes which have been collapsed along their longitudinal axes, so that a cross section presents the form of a figure eight. It can readily be understood that a considerable time must elapse before the acid can penetrate completely into the interior of such a tube so as to convert all its substance into gun-cotton.

For the same reason it will be understood that it must be very difficult to expel the last traces of acid from such capillary tubes, yet, if any trace of acid remains in them, it is likely to provoke progressive decomposition in the gun-cotton.

Von Lenk's process consisted in:

1st. *The cleansing and perfect dessication of the cotton.* The cleansing was effected by first removing the

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dirt and knots by mechanical means, then immersing the cotton in small portions, for two or three minutes, in a boiling solution of caustic potash (Sp. Gr. 1.021), in order to remove the fatty matters and incrusting substances, then removing the potash liquor by means of a centrifugal machine, and washing with pure water and, finally, drying at 95° F. At ordinary temperatures cotton wool exposed to the air absorbs 6 percent of moisture.

2nd. *The employment of the strongest acids attainable in commerce.* These consisted of nitric acid Sp. Gr. 1.48 to 1.49 at 17°.5 C and sulphuric acid Sp. Gr. 1.835 mixed in the proportions of one part, by weight, of nitric to three parts, by weight, of sulphuric.

3rd. *The steeping of the cotton in a fresh strong mixture of acids, after its first immersion and partial conversion into gun-cotton.* A pot holding about 60 pounds of the acid mixture was used for the dipping, and two skeins (about 3 ounces) of cotton were dipped at each operation. After some minutes, the partially converted cotton was removed from the pot, placed upon a rack and squeezed until one part of the cotton contained about ten and one-half parts of acid. The pressed cotton was now placed in a steeping pot and fresh acid poured over it, while the dipping pot was refilled to its original level with acid.

4th. *The continuance of the steeping for twenty-four to forty-eight hours.* After the gun-cotton had been placed in the steeping pot and the acid added, the gun-cotton was pressed to the bottom of the pot, so that it would be completely covered with the acid, the pot was then covered, placed in a trough of cool water and allowed to remain for the time stated.

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5th. *The thorough purification of the gun-cotton, so produced, from every trace of free acid.* To effect this the gun-cotton was placed in a centrifugal machine, revolving at about 800 turns per minute, and in about ten minutes the acid present was reduced so that one pound of the gun-cotton contained but three pounds of acid. The gun-cotton was then plunged into a cascade of water and washed in a running stream of water for from three to six weeks, and then treated with a weak solution of boiling potash, washed and dried in free air at 25° C. Then the gun-cotton was immersed for some time in a solution of sodium silicate (Sp. Gr. 1.072), wrung, and exposed for three days to free air, again washed, wrung and dried, first in free air, and finally in a chamber whose temperature did not exceed 35° C.

Von Lenk began the manufacture at Heitenberg, near Wiener-Neustadt, about 1853, and continued to direct the factory up to 1865, during which time considerable quantities of the material were made, and extensive experiments, on its value as a substitute for gunpowder as a projecting agent, were conducted with it, and the results were so favorable that in 1862 the Austrians supplied thirty batteries with gun-cotton cartridges, and the explosive bid fair to soon be adopted as a service explosive, but, unfortunately, two serious explosions during storage occurred, one at the magazine at Simmering in 1862, and the other at the magazine of Steinfeld in 1865, and these, combined with the fact that the explosive, in spite of the precautions taken, often developed abnormal pressures in the guns, led to its use being interdicted.

Von Lenk patented his process in England in 1862, and in 1864 the Prentice Brothers began the manufacture of gun-cotton under this process at Stowmarket. In 1865

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Abel patented his improvement on the process. This consisted in reducing the gun-cotton to a pulp, and then, by molding and pressure, converting it into such forms and masses as were desired for use. The pulping was effected by a rag engine or pulper, such as is used in converting the rags used in making paper into pulp. The advantage gained by this is, first, that the gun-cotton tubes are cut into such short lengths that the acid and foreign matters can be easily and completely removed from the fibre; second, that cotton waste, a cheaper material, can be used for the manufacture; and third, since the pulped material can be pressed, it is possible to impart to the final product a high density and thus obtain a large weight of the explosive in a small volume.

Abel's modifications were shortly afterwards adopted at Stowmarket, and the manufacture and use were successfully pursued without accident until August, 1871, when 13½ tons of the compressed gun-cotton, which was stowed in the packing-house at Stowmarket, exploded. A very thorough investigation of the circumstances attending this explosion was made, and, as a result, the jury found "that the accident was due to the spontaneous explosion of some impure gun-cotton, the impurity consisting in the presence of a large quantity of sulphuric acid, or of mixed sulphuric and nitric acids, which acids were wilfully added by some person or persons unknown, after the gun-cotton had passed through the regular process of manufacture and testing." Since then we have no record of any cases of spontaneous explosions having occurred, and it is very unlikely that they should have taken place, for, thanks to Brown's discovery, the finished product is now almost wholly stored in the wet state. Shortly after the Stowmarket explosion the English Government erected works at Waltham Abbey, and the French at Moulin-

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Blanc, and the other European governments followed suit, all of them adopting Von Lenk's process with Abel's modifications.

As has been said above, experiments were made in this country, not long after the discovery of gun-cotton, to test its value as a projecting charge in guns, but they were soon abandoned, as the material was found too unsafe for use in this way. Experiments were, however, begun again at this Station by Professor Hill in 1872 to test the value of the compressed gun-cotton, as made by Abel's process, for the use of the torpedo service, and these experiments were continued up to 1883, when on Nov. 14 of that year a gun-cotton torpedo outfit was issued to the U. S. S. Trenton and the material was adopted as a service explosive. The gun-cotton used in these experiments was obtained from Stowmarket, and that issued to the Trenton was in the form of cylindrical discs three inches in diameter and two inches high.

Having been adopted as a service explosive, it was not deemed prudent to depend upon foreign sources for our supply, so a plant for its manufacture was extemporized at this station, which was set in operation in March, 1884, and has been continued ever since, manufacturing as the needs of the Navy have required, so that, to-day, every ship in commission is supplied with her proper outfit, and we have stored in our magazines sufficient material to meet any immediate demands. Although this plant has been made to serve our purpose, yet it is not to be considered a model plant, while its location, as regards water supply and means of defence, and its arrangements, as regards safety, leave much to be desired.

We will now consider the chemistry of gun-cotton. This body, like the compounds referred to in the lecture on the picrates, is composed of carbon, hydrogen, oxygen

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and nitrogen, but it differs from them in the fact that while they are nitro-substitution compounds, this is a true salt, and belongs to the class of organic salts known as *esters*. It may be designated as cellulose nitrate, and the pure cotton fibre from which it is made is chemically known as cellulose. Owing to the fact that cellulose is a non-volatile solid, its vapor density has never been determined, and so its molecular weight, and hence its molecular constitution is unknown. Its ultimate analysis leads to the simplest empirical formula of $C_6H_{10}O_5$, but it is probable that its molecular constitution will be truly represented by some multiple of this expression. From its reactions cellulose may be regarded as a tribasic alcohol, the formula then being $C_6H_7O_2(OH)_3$.

Cellulose forms the principal ingredient of the cell membranes of all plants, so that it may be obtained from any of the multitude of existing plants, but the incrusting and other substances associated with the cellulose, as is readily seen by inspection, vary very much with the plant in which it exists, so that while wood sawdust and a variety of similar substances have been and are employed for the manufacture of cellulose nitrates, cotton has been found to be the source from which we could most easily and readily obtain an abundant supply of nearly pure cellulose. The purest cellulose which we meet with, however, is probably found in the so-called Swedish paper, which is employed in chemical laboratories for the purpose of filtration.

When cellulose is acted upon by nitric acid or mixtures of nitric and sulphuric acids, the hydrogen of the hydroxyl is replaced, more or less completely, by NO_2, and in this way various cellulose nitrates may be obtained. The composition of the products resulting from this action depends upon the strength of the acids employed, the

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proportions of acid used, the temperature during immersion, and the time of immersion. If the acids are as follows:

	Sp. Gr.	Parts by Weight.
HNO_3,	1.50	1
H_2SO_4,	1.85	3

the proportions of cellulose to acid is as 1 : 300, the time of immersion ten minutes, the time of steeping forty-eight hours, and the temperature about 15° C, then we ought to obtain the most complete conversion of the cellulose, and the reaction would be represented as follows:

$$(C_6H_7O_2)O_3H_3 + 3HONO_2 = (C_6H_7O_2)O_3(NO_2)_3 + 3H_2O.$$

The cellulose nitrate so obtained is familiarly known as the "trinitro-cellulose" and, according to Abel, it is the principle constituent of the military gun-cotton.

By the action of weaker acids, or other changes in the qualifying conditions, cellulose nitrates, in which less of the hydroxyl hydrogen is replaced, are obtained, and they are generally represented by the formula $(C_6H_7O_2)$-$O_3(NO_2)_2H$ and $(C_6H_7O_2)O_3(NO_2)H_2$, the bodies being called "dinitro-cellulose" and "mononitro-cellulose" respectively, and it is claimed that these lower compounds may be readily distinguished from the higher by the action of solvents upon them, the lower compounds being soluble in a mixture of common ether and alcohol, while the "trinitro-cellulose" is insoluble in this mixture.

From the difficulty attending the study of non-volatile bodies like cellulose and its esters, it is to be expected that differences of opinion will exist regarding their exact constitutions, hence we are not surprised to find that Vieille, from his researches, holds them to be more complex than they have, following Abel, been represented above. Vieille* regards cellulose as having the composi-

*Sur la force des Matieres explosive 2, 228; 1883.

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tion $C_{24}H_{40}O_{20}$, and by acting upon it with a mixture of the strongest nitric and sulphuric acids at 11° C, the cotton being to the acids as 1 : 100, or 150 by weight, he obtained $C_{24}H_{34}O_{20}(NO_2)_{11}$, called the endecanitrate, and which is completely insoluble in the mixture of ether and alcohol but completely soluble in ethyl acetate (acetic ether). Nitric acid (Sp. Gr. 1.502) alone gave $C_{24}H_{30}O_{20}(NO_2)_{10}$, the decanitrate, which was completely soluble in ethyl acetate and slightly soluble in ether-alcohol solution. With weaker acids he obtained successively $C_{24}H_{31}O_{20}(NO_2)_9$ the nononitrate, and $C_{24}H_{32}O_{20}(NO_2)_8$ the octonitrate, both of which were soluble in ethyl acetate and in ether-alcohol; the $C_{24}H_{33}O_{20}(NO_2)_7$, the heptanitrate, which gelatinized, without true solution, in ethyl acetate and ether-alcohol; the $C_{24}H_{34}O_{20}(NO_2)_6$, the hepanitrate, which swelled up in ethyl acetate without dissolving, and which was unacted upon by ether-alcohol; and, finally, the $C_{24}H_{35}O_{20}(NO_2)_5$ and $C_{24}H_{36}O_{20}(NO_2)_4$, the penta- and tetranitrates, which were obtained as friable pastes and were unacted upon by either the ethyl acetate or ether-alcohol When the acid was still more dilute the resulting product gave the iodine reaction for unconverted cellulose. As has been said, the "trinitro-cellulose" of Abel, or the endeca- and decanitrates of Vieille, are *gun-cotton*, the other cellulose nitrates being known as *pyroxylin*, and those of them which are soluble in ether-alcohol *collodion gun-cotton*. These latter are called collodion gun-cotton from the fact that the solution which they form with ether-alcohol, when exposed to the air, gives up its ether and alcohol by volatilization and deposits its gun-cotton as a gummy, colloidal, strongly adhesive film on the body with which it is in contact. This solution, known as collodion, is employed for coating the surfaces of the plates used in the wet process of photography, and it is also used in sur-

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While gun-cotton is a powerful explosive, and in fact a high explosive, *and necessarily dangerous as all explosives must be*, yet, when handled, used and stored as directed, it is the safest explosive known, and when in the condition in which it is issued from this station, it is wholly free from any tendency to undergo a dangerous decomposition. Partly owing to this fear which has existed, and partly owing to nature of the instructions given, there have been several instances reported where gun-cotton has been condemned and thrown overboard. In the majority of these cases I have been able to secure samples of gun-cotton from the same lots as those to which the condemned gun-cotton belonged, and I have been unable in any case to discover any indication whatever of dangerous decomposition.

When gun-cotton is decomposing it first begins to give off nitrous fumes and eventually yields them in such quantity as to color the surrounding atmosphere a deep brownish-red. At the same time the gun-cotton begins to show pasty yellow spots, and eventually the whole becomes converted into a pasty yellow mass which first shrinks to about one-tenth of the volume of the original gun-cotton and then swells up as the gas is evolved. Next the mass shrinks again and becomes converted into a gummy residue having a very much smaller volume than the gun-cotton from which it was formed, and finally it dries up to a brown horn-like mass. This decomposition results in the formation from the gun-cotton of oxides of nitrogen, formic and acetic acids which are evolved as vapors, and an amorphous, porous, sugar-like body almost entirely soluble in water, which contains a considerable quantity of glucose, gummy matter and oxalic acid, and a small quantity of formic acid, and of pectic and para- and metapectic acids. Changes such as these just described have re-

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peatedly taken place under my own observation with gun-cotton which has been imperfectly freed from acid, or with pyroxylin, and many other chemists have observed them, and in none of these cases did an explosion, or anything approaching an explosion, take place. The decomposing effects of acids may also be witnessed here on any Saturday while the gun-cotton factory is in operation, for it is the custom at that time to take the waste sweepings of the factory, which have accumulated during the week, to the beach, and to pour upon them a quantity of the waste acid mixture. Soon after the acid is poured on, the mass begins to evolve copious quantities of oxides of nitrogen (or, as as the workmen technically say, "firing" takes place) and the mass undergoes the changes described above, but no explosion ensues.

These observations have been made on gun-cotton decomposing when unconfined or when loosely confined. It is of course obvious that if the gun-cotton was confined in a tight receptacle the gases evolved during decomposition might generate pressure enough to burst the receptacle and thus produce an explosion. Again, as heat is produced by the chemical reaction, it might be possible that, when the gun-cotton is confined, the heat generated cannot be conveyed away as fast as generated, and that, in consequence, the temperature continually increases so that it eventually reaches the ignition point of the explosive, then, of course, an explosion might ensue, and this is the probable explanation of the origin of the explosions noted as occuring in the magazines at Stowmarket and elsewhere. The decompositions described have, with the exception of the destruction of the waste at this station, been observed to take place only in dry gun-cotton or pyroxylin. To produce it in wet gun-

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cotton it is necessary that the amount of acid present should be very much in excess of the gun-cotton with which it is in contact, hence the development of slight traces of acid during the storage of wet compressed gun-cotton, as has been observed by Abel, is not likely to produce dangerous decomposition, while besides the water present tends to prevent any considerable rise in temperature.

It is well-known that light rays sometimes play an important part in inducing chemical change to take place. We have only to cite the well-known cases of the decomposition of carbon dioxide within the leaf-cells of plants, or of the silver salts in the photographic plate, or better, we can recall the decompositions of the amides as noted in our lecture on the fulminates. It is not to be wondered at that it should be believed and expected that gun-cotton would also be susceptible to the action of light, especially since Tyndall has shown* that nitrous esters like the amyl and butyl nitrites may be decomposed by the action of a beam of light.

The literature of gun-cotton and pyroxylin is full of the most conflicting statements regarding the effect of light upon them, but this is not surprising when we consider the great variety of substances employed and their varying degrees of purity as made by many different methods. The most searching and exhaustive examination of this question has probably been made by Abel, and we quote his conclusions.†

Gun-cotton produced from properly purified cotton, according to the directions given by Von Lenk, may be exposed to diffused daylight, either in open air or in closed vessels, for very long periods without undergoing any change. The preservation of the material for three

*Heat as a Mode of Motion 478; 1879.

†Phil. Trans. 157, 250; 1867.

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and one-half years under these conditions has been perfect.

Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in gun-cotton of the description defined above; and the statements which have been published regarding the very rapid decomposition of gun-cotton when exposed to sunlight do not therefore apply to the nearly pure cellulose nitrate obtained by strictly following the system of manufacture now adopted.

If gun-cotton in closed vessels is left for protracted periods exposed to strong daylight and sunlight in a moist or damp condition, it is affected to a somewhat greater extent; but, even under these circumstances, the change produced in the gun-cotton by several months exposure, is of a very trifling nature.

Singularly enough it has been found that gun-cotton, which had been freely exposed to air and diffused sunlight for about twelve months, had its stability, as determined by the heat test, very materially raised.

Gun-cotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed into boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary storehouses (as far as an experience of three and one-half years has shown.)

Gun-cotton prepared and purified according to the prescribed system and stored in the ordinarily dry condition, does not furnish any indication of alteration, beyond the development, shortly after it is first packed, of a slight peculiar odor, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

Abel has also studied the effects of heat upon both dry and wet gun-cotton, and he finds* that the influence ex-

*Loc cite p. 251.

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erted upon the stability of gun-cotton of average quality, as obtained by strict adherence to Von Lenk's system of manufacture, by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates, is very trifling, and it may be so perfectly counteracted by very simple means, which in no way interfere with the essential qualities of the material, that the storage and transportation of gun-cotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident, than is the case with gunpowder.

Perfectly pure gun-cotton resists to a remarkable extent the destructive effects of temperatures, even approaching 100° C, and the lower cellulose nitrates (soluble gun-cotton or pyroxylin) are at any rate not more prone to alteration, when pure. The incomplete conversion of cotton into the most explosive product does not, therefore, of necessity result in the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid mixture.

But all ordinary products of manufacture contain small proportions of organic nitrogenized impurities, of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matters retained by the cotton fibre, and which are not completely separated by the ordinary, or even a more searching process of purification.

It is the presence of this class of impurity in gun-cotton which first give rise to the development of free acid, when the substance is exposed to the action of heat; and it is the acid thus generated which eventually exerts a destructive action upon the cellulose products, and thus establishes decomposition which heat materially accelerates. If the small quantity of acid developed from the

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impurity in question be neutralized as it becomes nascent, no injurious action upon the gun-cotton results, and the great promoting cause of the decomposition of gun-cotton by heat is removed. This result is readily attained by uniformly distributing through gun-cotton a small proportion of a carbonate; the sodium carbonate, applied in the form of a solution, being best adapted to this purpose.

The introduction into finished gun-cotton of one per-cent of sodium carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated temperature as would induce some decomposition in the perfectly pure cellulose products. That proportion affords, therefore, security to gun-cotton against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to gun-cotton might exert upon its properties as an explosive, would consist of a trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

I have observed that when dry gun-cotton is freely exposed to air in an atmosphere of a temperature of about 45° C for about three months, its stability, as determined by the heat, is materially raised just as Abel found it to be for exposure to diffused daylight.

Water acts as a most perfect protection to gun-cotton (except when it is exposed to sunlight), even under extremely severe conditions of exposure to heat. An atmosphere saturated with aqueous vapor suffices to protect it from change at elevated temperatures, and wet or damp gun-cotton may be exposed for long periods in

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confined spaces at 100° without sustaining any change.

Actual immersion in water is not necessary for the most perfect preservation of gun-cotton; the material, if only damp to the touch, sustains not the slightest change even if closely packed in large quantities. The organic impurities, which doubtless give rise to the very slight development of acid when gun-cotton is closely packed in the dry condition, appear equally protected by the water; for damp and wet gun-cotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from the gun-cotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient, not only to act as a perfect protective, but also to guard against all risk of accident. It is therefore in this wet condition that all reserve stores of the substance should be preserved, or that it should be transported in large quantities. If the proper proportions of sodium carbonate be dissolved in the water with which the gun-cotton is originally saturated for the purpose of obtaining it in this non-explosive form, the material, whenever it is dried for conversion into cartridges, or employment in other ways, will contain the alkaline matter required for its safe storage and use in the dry condition in all climates.

Cold has no effect upon dry gun-cotton, but, of course, if low enough, it may freeze the water in the wet gun-cotton, and when the latter is in the form of compressed pulp, as now issued, the freezing will cause flaking, cracking and breaking down of the physical structure with a consequent reduction in density, hence freezing is to be avoided if possible.

Alternate changes from heat to cold and the reverse,

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unless excessive, have little effect on the physical structure and none on the chemical stability of gun-cotton.

Gun-cotton is not susceptible, even when dry, to pressure, percussion or friction, unless it be strongly confined and firmly compressed, and the heat developed is very considerable. To explode dry gun-cotton, by percussion, with some degree of certainty, it is necessary to take a very small piece, wrap it tightly in tin foil, place it on an anvil, strike it several light blows to compress it, and then a heavy blow. If the latter is not fair it will fail to effect the result. As will be seen later, shell filled with discs of dry compressed gun-cotton have been fired from 24-pounders with service charges of powder into the masonry escarpment of the fort on Rose Island at a distance of 50 yards from the muzzle of the gun, where the shell were completely broken up on impact without any of the gun-cotton having been exploded. The wet gun-cotton is in the process of pressing subjected to a pressure of about 6300 pounds per square inch, and the pressure has been carried to over 13000 pounds without causing explosion.

If a flame or any incandescent body is applied to dry loose gun-cotton, the latter burns with a flash but without explosion. If the cotton is woven or twisted tightly, the speed of combustion is very much reduced, and when the gun-cotton is pulped and compressed, the rate of combustion is reduced still more. If water is poured on a disc or block of burning gun-cotton, the flame may be extinguished, though sometimes, when the fire is inside, it can be reached only with difficulty. If the mass of burning gun-cotton is very large, it is possible that an explosion may take place from the outer parts furnishing sufficient confinement to the inner. Wet compressed gun-cotton cannot be set on fire until the moisture is

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dried out of it. If a wet disc or block be placed in a fire, the outer surface will dry and be slowly consumed, and this will continue, layer by layer, until the whole is consumed. It is a common experiment here to place a magzine box filled with wet gun-cotton in a fierce bonfire and let it burn away, taking out some of the burning discs and extinguishing them by rolling on the ground or plunging in water, and subsequently exploding them by detonation. As much as 2000 pounds of wet gun-cotton has been placed at one time in a bonfire, where it slowly burned away without explosion.

The point of explosion of gun-cotton and pyroxylin naturally vary somewhat, but that of gun-cotton may be taken as about 182° C (360° F). The Stowmarket test required that it should be above 172° C.

From what has been said with respect to the products of explosion of gunpowder, it might be expected that those furnished by gun-cotton would vary according to the conditions under which the explosion takes place. When a mass of the gun-cotton wool is exploded in an unconfined state, the explosion is comparatively slow (though appearing to the eye almost instantaneous) since each particle is fired by the flame of that immediately adjoining it, the heated gas (or flame) escaping outwards, so that some time elapses before the interior of the mass is ignited. But when the gun-cotton is enclosed in a strong case, so that the flame from the portion first ignited is unable to escape outwards, and must spread into the interior of the mass, this is ignited simultaneously at a great number of points, and the decomposition takes place far more rapidly; a given weight of gun-cotton being thus consumed in a much shorter time, a far higher temperature is produced, and the ultimate results of the explosion are much less complex, as would be

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expected from the well-known simplifying effect of high temperatures on chemical compounds. The determination of the products of explosion of confined gun-cotton was effected by Karolyi by enclosing the gun-cotton in a cast-iron cylinder, strong enough to resist bursting, until the combustion of the last portion of the charge, which was suspended in an iron globe exhausted of air, and exploded by a galvanic battery; the total volume of the resulting gases was then measured and subjected to analysis. Unfortunately the cellulose nitrate used by Karolyi was not pure gun-cotton, so his results are but roughly approximate, still they indicate that the reaction might proceed according to the following equation:

$$2(C_6H_7O_2)O_3(NO_2)_3 = 9CO + 3CO_2 + 7H_2O + 3N_2.$$

although, naturally, no single equation would be likely to represent the complex reactions involved in an explosion by ignition. From this equation we deduce that one gram of gun-cotton yields 829 $\frac{c}{cm}$ of gas at 0° and 76 cm., or, with one cubic centimeter of compressed gun-cotton having a density of 1, one volume of this gun-cotton would yield 829 volumes of gas.

The quantity of heat generated in the explosion of gun-cotton, according to Roux and Sarrau, is 1056.3 centigrade units. The specific heat of the products of explosion is 0.2855, and this gives the temperature of the gas at the moment of explosion as 3700° C. At this temperature the 829 volumes become expanded to 12064, exerting a pressure of 81 tons per square inch if the density of gun-cotton is 1. The experiments of Nobel and Abel have indicated 4400° C as the temperature of explosion, and a pressure considerably more than double that produced by gunpowder when fired in a space which is entirely filled by the charge. Sarrau and Vieille found

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that at the high pressures the water was dissociated, more of the carbon dioxide being formed. Using Vieille's formula this may be represented by the equation

$$2C_{24}H_{29}O_{20}(NO_2)_{11} =$$
$$24CO_2 + 24CO + 12H_2O + 17H_2 + 11N_2,$$

and by calculation we find that the initial pressure exerted by gun-cotton is over three times that of gunpowder, and that, like that of gunpowder, the effect is reduced in practice by the incomplete state of combination of the elements and the complexity of the products which they tend to form, and the result is that the impact becomes less brusque and more regular as the combination becomes more complete during cooling.

The value of gun-cotton as a military explosive was much enhanced by the discovery, made in 1868 by E. O. Brown of the Chemical Department at Woolwich, that it could be detonated, even when unconfined, by means of a small charge of mercury fulminate, and that it could even be so detonated when thoroughly saturated with water, if only a small initial charge of dry gun-cotton be detonated in contact with it, and this is the method which is now universally used for producing the explosion of compressed gun-cotton, for not only is it easy of application and enables us to explode gun-cotton when wet, but it causes the explosive to develop its maximum force in a very small interval of time, and thus to produce that crushing effect which is desirable in a torpedo explosive. Berthelot estimates the pressure produced by the detonation of gun-cotton of density 1.1, when in contact, to be 24000 atmospheres, or about 160 tons per square inch, which is one-half the pressure estimated for mercury fulminate. Sebert finds the rate of propagation of the detonation, when the gun-cotton is confined in

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tubes of tin, to be from 5000 to 6000 meters per second, while it is but 4000 in tubes of lead. Piobert found the rate of inflammation in flocculent gun-cotton in free air to be eight times that of gun-powder.

From our experiment we have found that thoroughly dry gun-cotton may be detonated by three grains of mercury fulminate, and air-dried gun-cotton by five grains, provided the fulminate is well confined in copper cases, and the cases are *in intimate contact* with the gun-cotton. These conditions are important to success. Notwithstanding so small a quantity can effect the detonation, we use thirty-five grains in our service detonators, and I would most urgently advise that the amount should not be reduced, for the detonator is the soul of the torpedo, and if it fails to do its work the whole system fails. Our service detonators do not contain so large a charge of fulminate as to make the risk of storing, transporting and using them extra hazardous, while they are so cheap that by our present expensive methods of manufacture they are invoiced at but 11 cents apiece. On the other hand it is probable that in action a spar torpedo will be put in position to do damage to the enemy only after the the exposure and probable expenditure of many lives and much property, and it is essential that when in place it shall fire without fail. On these grounds I urgently advise that we should always have a large co-efficient of assurance.

We have noted that when gun-cotton is detonated it exerts a pressure in contact of 24000 atmospheres, and that it may be detonated when freely exposed in air. If a mass of compressed gun-cotton be placed on an iron plate in the open and detonated, we will find a marked impression produced on the iron plate, provided the latter is thick enough to resist rupture, and this impression is

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an exact reproduction of that face of the gun-cotton which was in contact with it. If there are cavities in the face of the gun-cotton similar cavities will be produced in the iron plate, and by increasing the size of these cavities until I have bored holes through the gun-cotton, I have been able to increase the cavities in the iron plates until I have perforated them. Several theories have been advanced to account for this phenomenon, but I hold it to be a ballastic one. Where the gun-cotton is in physical contact with the plate, we have a statical pressure, but where there are spaces we have the gun-cotton above them or the products of its explosion projected through these spaces and impinging on the underlying plate thus producing a kinetic pressure which probably produces erosion.

When gun-cotton, or any other high explosive, is tamped we obtain a more violent disruptive effect, through its detonation, than when it is untamped, for confinement brings about the most complete decomposition. We speak of it as untamped when freely exposed in the air, but this is not strictly true with a high explosive for it acts so quickly as to violently disturb and set in motion a very considerable mass of the atmosphere, and this atmosphere acts as a tamp.

Wet gun-cotton appears to be a more violent disrupting agent when detonated than dry gun-cotton is, notwithstanding that its combustion is not so complete. I explain this by supposing that the water in its pores, being nearly incompressible and highly elastic, increases the rate of propagation of the explosive reaction, and hence diminishes the time factor.

Gun-cotton may be exploded by influence — that is one mass may be detonated by the detonation of another mass not in actual contact with it. We may demonstrate this

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by placing discs of gun-cotton on an iron beam, separated by intervals of from a quarter to one inch, and detonating one of the discs, when the impressions of the others will be found on the underlying iron, provided the experiment is properly conducted. The effect is increased with the size of the initial charge and diminishes as the distance separating the masses. It depends too upon the medium which propagates the shock and the sensitiveness of the mass to be exploded. Explosion by influence is employed in countermining.

Reference books, *Hill's Notes, Proc. U. S. Naval Inst., Berthelot's Sur la force des Matieres Explosives, Desortiaux's Traité sur la Poudre, Bloxam's Chem., Abel, Phil. Trans.* 156, *269* and 157, *181; Majendie's Explosion at Stowmarket 1872, Richardson and Watts Chem. Tech.* 1 [4], *443;* 1867.

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LECTURE VIII.

GUN-COTTON—STATION METHODS OF MANUFACTURE AND TESTING.

The cotton used at this Station is the kind known as "weaver's" or "cop" waste. It is the tangled clippings from the spinning room, and is received in bales containing about 500 pounds each. This form of cotton is preferred to cotton "wool" on the ground that the thready form prevents the material from packing closely together when wet by the alkaline solutions, water or acids used in the various processes through which it is passed, and thus permits of more complete, uniform and speedy treatment, while it diminishes the chances of fuming during "dipping." Besides the original cost of the waste is less than that of cotton of a marketable length. The waste as received contains knots, "cops"(small pieces of paper upon which the thread is wound), dirt and oil from the machines, together with incrusting substances, naturally existing on the fibers, and hygroscopic moisture, all of which must be removed before the material is subjected to the nitrating process. Hence the first step is the manual sorting of the waste to remove the larger foreign bodies

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such as nails, pebbles, bits of wood, metal and paper, which are sometimes found in it, and then the waste passes to the

FIRST BOILING—TUB.

This is a covered tub which is heated by live steam, as shown in Plate 1. The tub is made of white pine and has a capacity of 500 gallons. Two hundred (200) pounds of cotton are placed in the tub, to which 250 gallons of water and 35 pounds of caustic soda are added, the steam is turned on, and the whole maintained at the boiling point for eight hours. The liquid is then drained off from the cotton, which remains thus over night, when the tub is filled with clear water and the boiling continued for eight hours more and again drained over night. By the manual picking the larger masses of foreign bodies have been removed. By the boiling with alkali the oils are saponified, and the soap formed acts as a detergent and removes much of the dirt, while the boiling alkaline solution acts also as a solvent for the incrusting matter. This process affects the fibre, for by prolonging the boiling with the alkaline solution or increasing the amount of alkali the fibre is materially weakened, and advantage may be taken of this to facilitate the operation of pulping, but the gain in this direction does not compensate for the loss in the product, while the hot, strong, alkali solution rapidly destroys the tub.

From the first boiling-tub the wet cotton passes to the

FIRST CENTRIFUGAL WASHER.

This is a machine of the ordinary form and construction, as shown in Plate 2, being 26 inches in diameter, ¼ inch mesh, and making about 1400 revolutions per minute. From 6 to 7 pounds of the cotton are put in

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the centrifugal at a charge, the wringer is set in revolution and a stream of fresh water is turned on the cotton and allowed to play upon it until the slippery feeling (due to the alkali) has disappeared. This operation requires about 8 minutes, and the washing of the whole charge from the boiling-tub requires two hours.

From here the cotton passes to the

FIRST DRYING ROOM.

This is a room 5 feet 10 inches by 11 feet 4 inches and 11 feet high, the walls and ceilings of which are sheathed with asbestus paper. Around two sides of this room are nine rows of shelves or racks made of galvanized iron wire netting 1 to ½ inch mesh. Hot air enters the room from the final drier through a flue in one side and near the floor, which, after passing about and through the cotton on the shelves, issues by a ventilating flue at the top of the room. By the aid of the hot air the temperature of this drying room is maintained at a temperature of about 187° F. The cotton from the wringer is spread on the shelves in a layer about 2 to 4 inches thick, and it remains in this room, being turned every day, after the second day, until it is perfectly dry to the touch. The time of drying varies from three to five days.

From the drying room the cotton passes to the

PICKER.

This is the ordinary machine used in cotton mills, and, as seen in Plate 3, it consists of an endless flexible table upon which the cotton is fed, two small horizontal cylinders, armed with teeth, rotating in opposite directions, as shown by the arrows, and a large wooden drum which is also armed with teeth.

As has been said, the cotton waste, as received, is

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badly tangled and contains many knots and rolls. It can be readily understood that the stirring and boiling, produced by the live steam in the boiling-tub, tends to tangle the mass still more. The complete conversion of the cellulose depends to a large degree upon the form of the cotton when it goes into the acid. If knots and rolls be present in the cotton they produce more or less "firing," and they are more or less yellow after the conversion. The picker serves to straighten out the tangled mass and open up the knots and rolls, so that the acid may have ready access to the fibre, but the cylinders of the picker should be so adjusted that the thread is not torn apart during this process. It takes about two hours to pass 200 pounds of cotton through the picker, and it results in about three pounds of loss.

The cotton passes from the picker to the

FINAL DRYING CLOSET.

This apparatus, which is shown in Plate 4, consists of a large closet 6 feet 7½ inches long, 4 feet wide, and 5 feet 4½ inches high, made of galvanized iron, which contains two sets of six drawers, each 2 feet wide, 3 feet 10 inches long, and 4 inches deep, made of the same material, with the exception of the bottoms, which are made of galvanized iron wire netting of ½ to 1 inch mesh. These drawers are 5 inches apart vertically with a sheet of $\frac{4}{16}$ inch galvanized iron between them which serves to deflect the current of heated air.

Air, which has been drawn over a steam radiator, is driven into this closet by means of a No. 4 Sturtevant blower, and led about and through the cotton out to the first drying room. By means of this hot air the temperature of the closet is maintained at about 225° F, but has varied from 200° to 260° F.

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The cotton from the picker, which contains from 6 to 10 percent of moisture, as all atmospherically dry cotton does, is spread over the drawers in a layer about 4 inches thick, and the drawers are then closed. The cotton is allowed to remain in this drying closet for eight hours, at the end of which time it is estimated to contain from .25 to .50 percent of moisture.

One-half of one percent is the largest amount of moisture which gun-cotton may contain at the time of dipping. With a larger amount, even if it only reaches to one percent, a reaction takes place by which unstable compounds are formed which are not removed by the subsequent treatment which the gun-cotton undergoes. It is stated that an amount of moisture which is seriously objectionable, when present in the cotton at the time of dipping it in the acids, may be present in the acids in which the cotton is dipped without material harm to the process or product.

In order that the highest nitric ester may be obtained, it is essential that the cotton at the time of dipping should be pure, dry and cool. Hence, in order to cool it out of contact with the air, it is packed directly from the drawers of the final drying closet, and, while yet hot, into service powder tanks, the covers of which are screwed on air-tight, and then the whole is allowed to stand in a cool room over night. The 150-pound powder tank holds about ten pounds of cotton when filled by hand pressure. The tanks containing the cooled cotton are then transported by the railway to the

DIPPING OR CONVERTING ROOM.

This room contains the dipping troughs, acid reservoirs, digestion pots and cooling troughs. The

DIPPING TROUGHS

Are shown in section at the right hand of Plate 5. Five

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of these, each having a capacity for about 150 pounds of mixed acids, are used. They are made of cast iron, and are set in an iron trough in which cold water circulates, which serves to keep the acid below 70° F during the process of conversion. At the rear and top of each trough is an iron shelf or grating, upon which the partially converted cotton is squeezed, and above this is an iron rod to which the hook in the end of the lever press is attached during the process of squeezing. Only four of the troughs are used for dipping the cotton in, the first being used as a reservoir for acid for immediate consumption. The troughs are placed side by side under a wooden hood, and a flue in the rear of this hood leads the acid fumes evolved into a vacuum chamber at the rear which connects with the suction pipe of the ventilating fan that ejects the fumes through a flue in the roof of the factory.

ACIDS.

The acids employed in the manufacture are purchased according to the following specifications:—

SPECIFICATIONS FOR MIXED ACID.

The Mixed Acid to consist of one part, by weight, of nitric acid to three parts, by weight, of sulphuric acid.

The Nitric Acid must have a real specific gravity of not less than 1.5, at a temperature of 15° C., and be free from chlorine and its compounds. The color must not be darker than straw. The acid must not contain sulphuric acid in sufficient quantities to perceptibly raise the specific gravity.

The Sulphuric Acid must have a real specific gravity of not less than 1.845, and be clear and colorless.

Proposals for furnishing the above must include the delivery of the mixed acid f. o. b. at Newport.

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The acids are delivered in wrought iron cylindrical drums 3 feet 3 inches long, 28 inches in diameter, and 1 inch thick, and each holding about 1200 pounds of mixed acids.

With our present knowledge of the mixed acids there is no certain method of inspection except by the Chemist from the Station making an examination of the separate acids at the acid works before the acids are mixed, and then supervising the mixing. A thorough study of the question will undoubtedly enable us to discover means for determining whether or not the mixed acids received conform to the specifications, but this has not yet been done. A preliminary investigation has, however, shown that the specific gravity of the mixed acids is not the mean specific gravity of the components, and that a contraction in volume has taken place. The examination is complicated by the fact that the acid as received contains a white, finely divided solid in suspension which does not settle out completely until standing for two weeks or more. To remove it by filtration is in the nature of things a difficult operation, but my Platinum Felt Filter* bids fair to enable us to surmount this difficulty. This suspended solid appears to be a basic sulphate of iron resulting from the slight action of the acids on the metal of the drums. Notwithstanding this action these drums offer us the cheapest, safest and altogether the most practical means of transporting these acids. Before their use the separate acids were brought to the Station in glass or acid-proof stoneware carboys and mixed when desired for use. While this method gave a better check on the quality of acid delivered, the serious fires and accidents which resulted from breakage during transportation led to its abandonment.

*Jour. Anal. Chem. 2, 241-243; July, 1888.

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The acid from the drums is pumped into large acid-proof stoneware reservoirs in the dipping room, and from there it is led by a conductor into the dipping troughs.

DIPPING THE COTTON.

The cotton is weighed out, as used, in one pound lots. This is then divided into three nearly equal parts which are successively and rapidly worked into the acids in the dipping trough by means of the steel fork shown in the extreme left of Plate 5, the separate portions being well stirred about in the acid to prevent any local rise in temperature. When the whole is immersed a 10-minute sand glass is turned and the "dipper" passes on to the next trough where this operation is repeated. By the time he has filled the fourth trough with its charge the sand has run its course above the first trough, so this charge is withdrawn from the acid, placed upon the grating and squeezed by the lever press as completely as possible and then placed in the digestion pot.

LEVER PRESS.

This is an iron bar about 5 feet long having a hook at one end. A plate is attached to the bar by a pivot about 8 inches from the hook. To use the press the hook is attached to the rod above the dipping trough, the plate is placed on the cotton and pressure is applied to the longer end of the lever. The device is shown in the center of Plate 5.

DIGESTION POT.

This is an ordinary two-gallon crock made of coarse stoneware, glazed inside and out, and provided with a cover, as shown in the center of Plate 5. It is of the first importance that the pot should be sound and the glaze intact so that no leakage can take place, for if

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moisture should reach the charge in the crock the latter would be "fired." Immediately before use the pots are wiped out with a little acid so as to remove any moisture which may have accumulated or condensed on their walls. This process is technically known as "drying-out."

The mass of partially converted cotton saturated with acid weighs, as placed in the pot, from 10 to 12 pounds. When it is put in the pot it is squeezed down compactly by means of the hand press shown at the left of Plate 5, the pot is then covered and placed in water in the cooling trough where it remains over night. A gang of two men can thus treat 100 pounds of cotton in a working day of 8 hours.

COOLING TROUGHS.

These are made of wood 2 inches thick, are rectangular in shape, are lined with lead and provided with a water tap at one end and an overflow pipe at the other. The latter pipe is just high enough and of such size as to prevent the water in the trough from rising above the level of the acid and gun-cotton in the pots. The troughs are 1 foot 5 inches wide, $8\frac{1}{2}$ inches deep, and 24 feet 6 inches long. Each one will hold 20 pots. Six are used and one is reserved for emergencies. Cold water is kept circulating through these troughs in summer, but in winter they are simply filled with water.

From the cooling troughs the gun-cotton passes to the

ACID WRINGER.

This is a centrifugal wringer made of mild steel and provided with a cover to prevent the acid or acid fumes from escaping. The wringer is 20 inches in diameter and 9 inches deep, has a $\frac{1}{8}$ inch mesh and makes 1400 revolutions per minute. This wringer is shown in Plate 6, and from this we see that it is provided with a flue

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leading to the ventilating fan by which the fumes are driven into the outer atmosphere, while a pipe from the bottom leads the extracted acid into a receiver in the factory cellar. Before using for the day this wringer is "dried out" by pouring in a pitcher-full of acid and rotating the basket.

Two pots full of gun-cotton are wrung at one operation, and this occupies from three to four minutes. The operation should be conducted with caution, and extreme care should be taken that no moisture or oil reaches the mass. As the digestion pots have been immersed in water in the cooling troughs, it is necessary to let them drain and to dry their outer surfaces before taking them to the acid wringer. Several explosions or "firings," which have taken place in wringers, have been traced to drops of oil from the machinery, or of perspiration from the faces of the workmen, which have fallen on the gun-cotton.* The wrung gun-cotton is taken from the wringer by hand, the hands being covered with rubber gloves, and it then passes to the

IMMERSION TUB.

This is a wooden tub of 800 gallons capacity provided with a perforated false bottom, and having a $3\frac{1}{2}$ inch inlet and a $3\frac{1}{2}$ inch outflow pipe. At one end is a wooden drum 2 feet in diameter provided with feathers, and placed so as to be nearly one-half immersed in the water of the tub when the tub is filled. This cylinder rotates horizontally about its axis and serves as a beater to carry the gun-cotton under the water. Above the tub and at one side of the beater is placed a wooden box or hopper, lined with lead, which is provided with a door in the side through which the gun-cotton is introduced into the

*Proc. Nav. Inst. 13, 417–418; 1887.

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hopper, and a slot in the bottom by which the gun-cotton is fed to the tub. The whole is shown in Plate 7.

The object of the immersion process is to wash out the greater portion of acid from the gun-cotton. As stated above, a small quantity of water is likely to cause firing, hence, to effect this washing successfully, it is necessary to use very small portions of gun-cotton at a time, to use very large quantities of water so as to drown the gun-cotton and to perform the operation so quickly that the acid is removed from the gun-cotton and distributed through the great body of water before any local heating can take place.

The course pursued is as follows: The tub being filled with water, the water flowing at full speed, and the beater being in rotation, two crocks of wrung gun-cotton are placed in the hopper. Then the workman inserts his hand protected by a rubber glove and, little by little, pushes the gun-cotton through the slot, and this operation is repeated until fifty crocks have been fed into the tub. When well washed the gun-cotton is placed in a wooden rack to drain. Owing to the scarcity of fresh water at this Station salt water is used in the immersion tub, so the gun-cotton from the tub is wrung out in a centrifugal wringer, like that shown in Plate 2, and washed with fresh water until the salty taste has disappeared. Two crocks full are wrung at a time, and three washings are generally sufficient.

No matter how much the gun-cotton is washed in cold water it still retains acids or easily decomposed material which can only be removed by boiling, hence, from here the gun-cotton passes to the

SECOND OR GUN-COTTON BOILING TUB.

As shown in Plate 8 this consists of a wooden tub of

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300 gallons capacity, which is provided with a perforated false bottom and heated by a steam coil. The inlet pipe and coil are cut off from the interior of the tub so that the metal cannot come in contact with the gun-cotton. Here fifty pots of gun-cotton are boiled for eight hours in fresh water to which 10 pounds of carbonate of soda have been added, then drained over night, washed in a centrifugal wringer, like the one shown in Plate 2, with fresh water, returned to the boiling tub, boiled with fresh water for eight hours, again drained over night and again washed with fresh water in the centrifugal.

Then the gun-cotton passes to the

PULPER.

This machine, shown in Plate 9, is the ordinary "beater," "rag engine," or "Hollander," used in paper mills, and consists of a wooden tub 12 feet long, 5 feet wide, and 2 feet deep, with curved ends. The tub is partially divided along its longer axis by a wooden partition (of the same height as the walls of the tub) into two parts—the "working side," in which the gun-cotton is shredded between the knife edges on the revolving cylinder and those on the "craw," and the "running side," into which the shredded material is thrown by the revolving cylinder. The revolving cylinder is of wood, is 28 inches in diameter, 28 inches long, carries forty crucible steel knives and rotates two hundred times a minute. Under the cylinder is a massive oak block, called the "craw," the concave surface of which equals one-fourth the circumference of the cylinder. The side of the block leading to the curved face is gently inclined, while on the side beyond the curved face it is sharply inclined. In the center of the craw below the revolving cylinder is fitted a box of steel knives, and the cylinder is so ad-

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justed by set screws attached to the socket in which its shaft revolves that its knives just clear the bundle of knives in the craw. The cylinder is enclosed in a wooden cover, extending nearly the length of the partition, to prevent loss of the material by centrifugal action.

From 300 to 350 pounds of gun-cotton are slowly fed into the pulper, and water is added until, when the cylinder is revolving, the mass just reaches the top of the tub to the right of the cylinder, as shown in Plate 9. During the feeding the gun-cotton is held in a wall-pocket made of thin boards and canvas, which is placed at the left-hand end of the pulper. When the cylinder is set in revolution the gun-cotton is drawn between the knives and shredded and the paste forced over the craw where, as it flows sluggishly, it is heaped higher than at the other end of the tub, but it gradually flows to the other end, is drawn again between the knives, and so it continues until the whole of the gun-cotton is cut to the fineness of corn meal. When the pulper is in good working order this operation takes two days for a charge of the size stated above.

The mass is then run off into the

POACHER.

This is, as shown in Plate 10, a wooden tub similar in form to the pulper, but the cylinder is armed with wooden feathers instead of knives, and it serves simply to keep the gun-cotton in suspension in the water and to keep the whole mass in rotation about the tub. The poacher has a capacity of about 900 gallons. When the pulp has reached the poacher the gun-cotton is allowed to settle, and the water is drained off by means of a telescopic overflow pipe in one end of the poacher. The tub is filled with fresh water, the cylinder set in revolution

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and the circulation kept up for one hour, when the settling and draining is repeated, and these operations are continued for two days, making about six washings and settlings, when a sample is drawn and sent to the Chemist to be tested.

If the sample sent fails to pass the tests the washing in the poacher is continued until the gun-cotton will pass. When thoroughly washed the gun-cotton is again drained, three pounds of precipitated chalk, three pounds of caustic soda, three hundred gallons of lime water, and sufficient water to make the whole up to about 800 gallons, are added to it, and the whole is sucked up by means of a vacuum pump into the

STUFF CHEST.

This is a cylindrical iron vessel of about 850 gallons capacity fitted with a man-hole at the top, which is closed by a cover, which makes an air-tight fit, and provided at the bottom with an inlet pipe through which the pulp enters, and an outlet pipe through which the pulp is delivered. Through the center of the tank is a vertical shaft, which is provided with four feathers, and which is geared to a horizontal shaft above it. The object of this stirrer is to keep the gun-cotton and other solids uniformly suspended in the liquid so that the same proportions of each, as nearly as possible, may be always delivered to the molding press. The stirrer is run for about twenty minutes before the molding begins, and is kept in operation until the molding ceases.

The stuff chest rests upon stringers at the top of the factory so that its contents may gravitate to the press.

The pulp first goes, however, to the

WAGON.

Which is a cylindrical copper vessel of about 25 gallons

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capacity suspended by rollers upon a railway so that the top of the vessel just clears the oulet pipe of the stuff chest, while the bottom is well clear of the top of the molding press. Inside the wagon is a vertical stirrer, similar to that in the stuff chest and playing the same part, which is geared to a horizontal shaft that rotates between the rails. The pulp is delivered by an orifice in the bottom, which is closed by a valve which moves vertically and is operated by a lever and cord at the top of the wagon. A one-inch rubber tube one foot long is attached to the outlet of the wagon so as to assist in delivering the pulp at the desired point. The wagon is filled by rolling it under the stuff chest and opening the valve in the outlet pipe of the latter. The stirrer then being in rotation the wagon is rolled along until it reaches the molding press, when the rubber tube is led successively to each compartment of the molding press, the lever is pulled and the press is loaded. One wagon load serves for about three charges for the molding press.

MOLDING PRESS.

This is a hydraulic press made of bronze and containing four rectangular compartments 2.8 inches square with champfered corners, two of these compartments being shown in section in Plate 11. The press is closed by a block which is hinged at the back and locked at the front by a lever clamp swivelled eccentrically. The pistons have a 28-inch stroke. Through the center of each piston head is a rod $1\frac{1}{2}$ inch in diameter, which is screwed in the base of the press and reaches quite to the top, and which is used as the core to form the detonator hole in the gun-cotton block. The top of each compartment is closed by a plate perforated with holes through which the water, which is squeezed out of the pulp, escapes

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and flows into the reservoir between the compartments.

The finished gun-cotton block is 2.9 inches in diameter, $3\frac{7}{8}$ inches in diagonal (the corners being champfered) and 2 inches in height, and to produce this it is necessary that the molded block should be 2.8 inches in diameter, and $5\frac{1}{4}$ to $5\frac{1}{2}$ inches high, when the molding pressure is 100 pounds to the square inch. Knowing the size of the compressed block desired, it is determined, by experiment, how much of the pulp is necessary to produce it, the length of stroke of the piston being increased or decreased to produce this result. The pistons having been set, by means of the rod in the center of the piston heads, the pulp is run in until the compartment is filled, and this is repeated with each of the four compartments.

The perforated plates are inserted, the cover closed and locked, and the pressure applied. The pressing occupies about four minutes. When primers are desired only one-fourth the quantity of pulp is taken, and the molded blocks have but one-fourth the height of the service blocks.

FINAL PRESS.

This press, which is shown in side-view section in Plate 12, is one of Sellers' hydraulic presses, made of steel, with an 18-inch ram. On the head of the ram are nine pistons which fit neatly into nine apertures in the press block above them. The press block is made of gun-bronze, and it is 15 inches wide, 22 inches long and 7 inches thick. It is supported in place by being bolted to the vertical columns which support the head of the press. Above the press block is a traveling block which is hung by rollers on a horizontal track, so that it may be brought in close contact with the top of the press block, or pushed off from it at will. Two perforated steel plates which neatly fit the apertures in the

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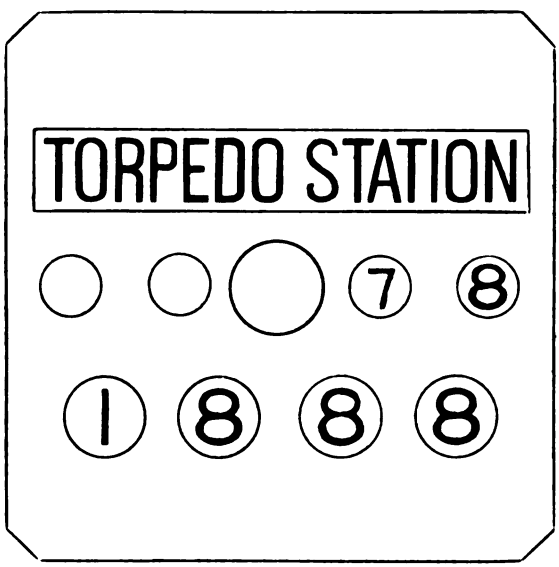
press block, are placed in each aperture, one, which is $\frac{1}{32}$ inches thick, above, and one, which is one inch thick, below the gun-cotton block, and these diaphragms serve to distribute the pressure uniformly over the surface of the blocks, while the perforations allow the water, which is squeezed from the block, to escape. The upper plate also bears on its lower surface the marks which it is desired to impress on the block, and thus serves as a die to stamp the gun-cotton. These marks are now as follows:



In which the figures recessed in the circles at the bottom record the year of manufacture (1888), and those at the right of the detonator hole the number of the factory charge (78). A very detailed account of the history of each charge is kept in the factory, and this method of marking enables us to keep track of each charge until it is expended. The two blank circles at the left of the detonator hole are for use when the number of the charge exceeds two figures.

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The press is loaded by rolling off the traveling block, lowering the pistons, dropping in the lower plates, then the molded gun-cotton blocks, then the upper plates, and, finally, rolling the traveling block back into place again. The pressure is then applied by means of a powerful hydraulic pump in a pit beside the press, the safety valve of which is set to discharge at from 1800 to 2000 pounds as indicated by the pressure gauge. Of course the total effect of the ram will be transmitted to the pistons and, as the area of the head of the ram is to that of the nine pistons heads as 3.4 : 1, the pressure per square inch on the gun-cotton will be 6120 pounds when the initial pressure is 1800, and 6800 pounds when the initial pressure is 2000. The pressure reaches the maximum about three minutes after the pump is set in operation, and this pressure is maintained for about one minute by the sand glass. When the ram is released the traveling block is rolled off, the pump is set at work again, and the finished blocks of gun-cotton are pushed to the surface of the press block.

When priming blocks are to be pressed, four of the molded blocks are inserted in each of the compartments of the press block, and they issue firmly compacted together, but showing distinctly the lines of demarcation of each of the molded blocks, and they may be readily split apart along these lines.

When the gun-cotton is taken from the final press it contains from 12 to 16 percent of moisture. It is but natural to apprehend danger from subjecting gun-cotton, which is so nearly dry, to the high pressures which are employed, especially when we consider that small particles of the substances might get pinched between the metal parts, and that some of these might become air-dried while the press is idle. Rumors of such explosions

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have reached us from abroad, but I have been unable thus far to verify any of them. However, no such explosions have thus far occurred at this Station, though the press block was once split open. As far as could be ascertained, this was due to the workman's having inadvertently inserted three of the perforated plates into one compartment and only one in another, thus causing the whole force of the ram to be exerted on one piston, which bent and jammed and finally split the block. The gun-cotton from this pressing was recovered intact from the press block.

To guard against serious results following an explosion here, the press is surrounded by a rope mantlet (such as was used in monitor turrets during the war of the Rebellion), which is braided from Manilla rope 1½ inch in diameter. There are four thicknesses to the mantlet, and this can be relied upon to arrest pieces of the metal if projected with not too great velocity.

When the gun-cotton blocks are taken from the press they are two inches in height, but after standing awhile they swell a little. Though, when taken out, they contain but from 12 to 16 percent of water, as sent into the service they contain about 35 percent. This is added by allowing the blocks to soak in a trough of fresh water until they cease to absorb water.

DRYING WET PRIMERS.

The blocks are packed in the torpedo cases at the gun-cotton factory as fast as they are made, the primer cases being filled with wet primers. A sufficient proportion of dry primers are sent with each outfit, and when the torpedoes are desired for use the wet priming blocks are withdrawn from the primer can and dry ones substituted. These wet ones are then dried by splitting the blocks

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apart into ½ inch portions, weighing each one, stringing them on a perfectly clean brass or copper rod or tube. separating the blocks one from another, and suspending the rod in a suitable dry place (not in the vicinity of the galleys or boilers) where they will be freely exposed to air and yet be under cover. The blocks are to be weighed separately from time to time, the weights being marked on each with a soft lead pencil, and they are to be dried until they cease to lose weight.

YIELD OF GUN-COTTON.

According to the equation on page 10, Lecture VII. we should obtain 183.3 pounds of gun-cotton from 100 pounds of cotton. If, however, we follow Vieille and consider gun-cotton as being cellulose endeca-nitrate, we should obtain, theoretically, 176 pounds of gun-cotton. In practice, notwithstanding the loss incident to the many manipulations, we obtain about 150 pounds of gun-cotton from 100 pounds of cotton taken from the final dryer. This makes about 7200 full sized blocks.

TESTING THE GUN-COTTON.

The gun-cotton, as drawn from the poacher, is submitted by the Chemist to two tests—the heat or stability, and the solubility tests. As it is of the first importance that the sample tested should represent the average composition of the charge in the poacher, the following course is pursued in

DRAWING THE SAMPLE.

About one quart of the pulp is to be drawn from the poacher, in very small quantities at a time, while the revolving cylinder is in operation and the pulp is circulating actively, portions being taken from both top and bottom.

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PREPARING THE SAMPLE.

The sample is allowed to stand until the gun-cotton has settled, when the water is poured off, and then one-half of the gun-cotton is wrapped in a thoroughly clean linen cloth and placed under a hand-screw press, where it is subjected to a tolerably severe pressure for about three minutes, or until water ceases to flow from it. The mass is then taken out in the form of a cake, which is broken up fine and rubbed up between the hands. About 200 grains of this gun-cotton are then placed in a paper tray which rests on the top of an oven heated to 120° F, care being taken that the tray does not come in contact with the walls of the oven, and the mass is thus heated with constant stirring for fifteen minutes. The dried sample is then transferred to a covered glass funnel with roughened sides, the neck of which is connected with a bellows, by means of which the finest particles of the gun-cotton are blown on the sides of the funnel, from which they are carefully removed. These fine particles, after exposure for two hours to the atmosphere of a normally warm and dry room, are weighed out for the heat test, twenty (20) grains being taken for this purpose.

HEAT TEST.

The materials required are:

1. Water bath.
2. Temperature regulator.
3. Thermometer.
4. Test tubes.
5. Test paper holders.
6. Glass rod.
7. Minute clock.
8. Test paper.
9. Glycerine solution.

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1. The water bath consists of a glass globe, about 8 inches in diameter, which is filled with water to within a quarter inch of the top when the water is heated. This globe is open at the top, and the mouth is closed by a cover of tin plate or brass. The cover is perforated with a small hole in the center to receive the thermometer, and with several holes about the central one of slightly larger diameter than that of the test tubes. To the bottom of each of these outer holes are fastened three spring clips inclined toward each other, so that when the tube is pushed through them they will close about it firmly and hold it in the desired position. The globe is placed on strips of wood in a copper bowl 10 inches in diameter, and the bowl is then filled with water. This outer bowl enables us to readily heat the apparatus without danger of breaking the glass globe, while the large mass of water assists in keeping the temperature constant for a considerable period of time. The whole apparatus is then placed on a support over a lamp which should be controlled by a Scheibler temperature regulator or thermostat.

4. The test tubes should be from $5\frac{1}{4}$ to $5\frac{1}{2}$ inches long, and of such diameter that each will hold from 20 to 22 $cm.^{-3}$ of water when filled to the height of 5 inches. They should be marked with a ring, drawn around them with a diamond, $2\frac{1}{2}$ inches from the bottom, and the gun-cotton should be compressed to the height indicated by this mark.

5. The test paper holders consist of small glass rods about 10 cm. long having a piece of platinum wire about 1 cm. long fused into one end, this wire being bent into a hook. These rods are passed loosely through holes in taper corks, the latter being of such size as to neatly fit the test tubes.

6. The glass rods are used for pressing the gun-cotton

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in the tube. They should be provided with flat heads and be long enough to easily reach to the bottom of the tubes.

8. The test paper used is that known as starch and potassium iodide paper, and it is made as follows:

Forty-five grains of white starch, which has been well washed in cold distilled water and thoroughly dried, are added to $8\frac{1}{2}$ ounces of distilled water, and the whole is heated to boiling, with constant stirring, and is kept gently boiling for ten minutes. Fifteen grains of pure potassium iodide (*i. e.* KI which has been recrystallized from alcohol) is now dissolved in $8\frac{1}{2}$ ounces of distilled water, and the two solutions are mixed and allowed to cool.

Strips or sheets of fine white filter paper, which have been previously washed in distilled water and redried, are dipped into the above solution and allowed to remain in it for not less than ten seconds, when they are removed and hung up to dry in a warm, dark room which is free from laboratory dust and fumes. When dry, the upper and lower margins of the strips or sheets are cut off and the paper is preserved in well stoppered bottles in the dark. The pieces of test paper used in making the test are about $\frac{4}{10}$ inches by $\frac{8}{10}$ inches (10 mm. by 20 mm.). They are attached to the test paper holders by piercing them near the top with the point of a penknife blade, two incisions being made at right angles to each other so as to form a cross. The point of the platinum wire is then inserted through the center of the cross, and the hook is bent firmly together so as to hold the papers rigidly in line with the rod of the holder.

9. The glycerine solution is made by dissolving ten percent of pure glycerine in distilled water. It is kept in a small bottle or flask the mouth of which is closed by a cork, and the latter is perforated to take a small rod or

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tube which is long enough to reach the bottom of the vessel. This rod is drawn to a point at its lower end. The glycerine solution is used to wet the test paper, and it is applied by holding the test paper holder vertically with the paper uppermost, and then touching the paper at the edge, where it is fastened to the platinum hook, with the rod which has just been drawn from the solution. Enough solution and no more must be applied to the paper than is sufficient to thoroughly wet it across its entire width and for one-half its length. The holder is held with the paper upward until the solution has been drawn by capillarity up to the middle of the paper and is found to go no further.

MAKING THE HEAT TEST.

The thermometer is inserted in the bath to a depth of $2\frac{3}{4}$ inches below the water, and the heat is applied until the temperature is constant at 150° F (65.°5 C.). The weighed sample of gun-cotton (20 grains) is put in the tube and pressed down by means of the rod to the mark, the tube is closed with a loosely fitting cork, and it is then inserted in the water bath until the bottom is $2\frac{1}{2}$ inches below the water level, *and the time of insertion is marked with the stop clock.* The test paper is now prepared, the paper being drawn up close to the bottom of the cork. The cork in the test tube is now removed and the test paper with its holder inserted in its stead. After the heating has gone on for a short time a thick film of moisture will begin to form in the upper part of the tube, and, when this is observed, the test paper is lowered by pushing the rod through the cork until the line of demarcation between the wet and dry portions of the paper are coincident with the lower edge of the ring of moisture, and the test paper is now closely watched. *When*

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the faintest sign of discoloration is observed on the test paper (and it appears at the line of demarcation between the wet and dry portions) *the time is marked again by the stop clock.* The elapsed time for stable gun-cotton should not be less than *fifteen* (15) *minutes.* If it be less the gun-cotton is rejected.

Simple as this operation appears, yet it is found to be difficult in application, and this is largely due to the difference in the readiness with which different observers, and especially untrained ones, can perceive the appearance of the brown coloration. So to assist them the following standard tint paper has been devised.

STANDARD TINT PAPER.

This is prepared by making a caramel solution in distilled water of such concentration that when diluted one hundred times (10 $_{cm.}^{-3}$ made up to a litre) the tint of this solution equals the tint produced by the Nessler test (2 $_{cm.}^{-3}$) in 100 $_{cm.}^{-3}$ of water containing 0.000075 grams of ammonia, or 0.00023505 grams of ammonium chloride. With the caramel solution lines are drawn on slips of white filter paper by means of a clean quill pen. When the marks thus produced are dry, the paper is cut into pieces of the same size as the test paper described above, and in such a way that each piece has a brown line across it near the middle of its length, and only those strips are preserved in which the brown line has a breadth varying from $\frac{1}{2}$ mm. to 1 mm. ($\frac{1}{25}$ to $\frac{1}{50}$ of an inch). This may be used by hanging a strip in a test tube beside the tube in which the test is being made and noting each until a brown line appears on the test paper similar to that on the standard tint paper.

PRINCIPLES GOVERNING THE TEST.

The principle upon which the use of the starch and

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potassium iodide paper is based may be shown by the following experiments with starch emulsion and iodine; starch, potassium iodide and chlorine; starch, potassium iodide and oxides of nitrogen; starch and potassium iodide paper and acids. From these we learn that the starch reacts with iodine to form a colored body. That when potassium iodide is decomposed in the presence of starch the iodine which is liberated reacts with the starch. That oxides of nitrogen and the nitrogen acids effect this decomposition. And that in the bath the heat drives off any free acids present in the gun-cotton, or decomposes any unstable bodies, and liberates nitrogen oxides or acids which react on the test paper.

SOLUBILITY TEST.

About 500 grains of the pulp from the poacher are treated in the hand press as described for the heat test, the cake is then broken up and placed in an air bath where it is dried at a temperature of 40° C for two or three hours, being rubbed between the hands occasionally to break up the lumps. When well dried it is removed from the bath and exposed to the air for an hour. Two grams are weighed out, placed in a flask and covered with four fluid ounces of a mixture of one volume of absolute alcohol and two volumes of Squibbs' strongest ether. The flask is corked and then shaken at intervals for two hours. The contents of the flask are now decanted upon a weighed linen filter (which has been previously washed in some of the ether-alcohol mixture) and washed on the filter with four ounces more of the ether-alcohol mixture, then the filter and contents are squeezed thoroughly to remove any of the solution present. The residue in the filter is replaced again in the flask, covered with four ounces of fresh ether-alcohol, corked and

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shaken at intervals for a half hour and again decanted upon the same filter as before and washed with four ounces more of the ether-alcohol. The filter and contents are then spread out on a plate of glass, placed in a drying oven and heated until the odor of the alcohol has completely disappeared. Then it is exposed to the air for two hours and weighed. The drying and exposure to the air should be repeated until the weight is constant.

The difference between the weight of the gun-cotton taken and the weight of residue found gives us the weight of the substance dissolved, and with this data the percentage is calculated. The soluble matter in the gun-cotton should not exceed 10 percent. As a matter of fact, the gun-cotton made here contains usually less than 6 percent.

The method described above is a commercial one and necessarily rough, while, besides, it is quite expensive. With alcohol at $1.50 per pound and ether at $1.00, it cost us about $3.00 for the solvent for each test. This method is followed now only because it was adopted from the English practice when the factory was first started, and I am not willing to make or propose changes in the methods existing here when I came until I have submitted the new ones to thorough experimental examination, and I have been prevented thus far from doing this by the pressure of the current work.

I have, however, made some few experiments with Szombathy's extraction apparatus and various solvents, and the results lead me to believe that we will find here a cheaper, quicker and more accurate means for the determination of the percentage of soluble matter.

The results of the tests are reported on the following form:

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TESTS OF GUN-COTTON.

Chemical Laboratory, Torpedo Station,

....., *188* .

Charge No. .....

SOLUBILITY.

	1.	2.	
Weight of gun-cotton taken.....	.....	.....	
" " filter.....	———	———	
" " gun-cotton + filter.....	.....	.....	
" " insoluble gun-cotton + filter..	———	———	
" " soluble gun-cotton.....	.....	.....	
Percent of soluble gun-cotton.....	.....	.....	
Mean			———

HEAT.

	1.	2.	
Time of starting.....	.....	.....	
" " stopping.....	———	———	
" elapsed.....	.....	.....	
Mean			———

....

(Passed.) *Chemist to Torpedo Corps.*

(Rejected.)

TEST FOR UNCONVERTED COTTON.

Besides the determination of the "soluble gun-cotton," it is sometimes necessary to determine the amount of unconverted cellulose present. This may be done by treating the residue from the ether-alcohol with ethyl acetate (acetic ether). By digestion with this solvent the cellulose nitrates are dissolved, and the unconverted cellulose is left behind and may be collected on a weighed filter. Or it may be treated, by boiling, with a solution of sodium stannite made by adding caustic soda to a solution of stannous chloride until the precipitate at first

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formed is just redissolved. This solution will also dissolve cellulose nitrates, but does not dissolve cellulose.

TEST FOR NITROGEN.

This may be most easily made by means of a nitrometer. There are various forms of this instrument, but Lunge's answers very well for the purpose. This consists of two glass tubes of about 150 $cm.^3$ capacity connected together by a long rubber tube. The upper end of one of the tubes is funnel-shaped, and there is a three way cock in the contracted neck between it and the tube. This tube, which is called the burette, is graduated into tenths of cubic centimeters, the other tube, called the filling tube, is plain. Both tubes are mounted in a burette holder so that they are vertical and side by side, but can be raised or lowered independently at will. Sufficient mercury is poured into the tubes to fill the graduated one completely, and the plain one partially when the latter is raised two-thirds its length above the graduated one. The stop cock of the graduated tube then being closed, the plain tube is lowered to place again. About .3 grams of thoroughly dried, finely divided guncotton are placed in the funnel and covered with 5 $cm.^3$ of pure concentrated H_2SO_4. The stop-cock is opened, the mixture is swept into the tube and washed in rapidly by about 10 $cm.^3$ more of the acid, care being taken that the flow of acid is constant, so that no air gets into or gases escape from the tube, and the stop-cock is closed. Action begins as soon as the mixture reaches the mercury according to the following equation:

$$(C_6H_7O_2)O_3(NO_2)_3 + 9H_2SO_4 + 18Hg =$$
$$2(C_6H_7O_2)O_3H_3 + 9Hg_2SO_4 + 6H_2O + 6NO,$$

and the NO gradually collects at the top of the tube and displaces the mercury. This action is assisted, from time

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to time, by removing the tube from its clamp and shaking it, care being taken that none of the gas or acid gets into the rubber tube. After all action ceases (which usually is about one-half hour) the tubes are adjusted so that the mercury in each is at the same height, then the filling tube is raised so that the level of the mercury in it is higher than that of the mercury in the burette by one-seventh of the number of divisions in the burette occupied by the sulphuric acid, and then the volume of the gas is read off. The apparatus is allowed to stand fifteen minutes and then read again, several readings being made by moving the tube and readjusting it again. When the readings are constant, the thermometer and barometer are noted and the volume of the gas reduced by Charles' and Mariotte's laws to 0° C and 76 cm. Then the weight of nitrogen present, and hence the percent in the gun-cotton taken is calculated from this volume by the methods and data given in Lectures I, II and III. If we assume the formula for military gun-cotton to be $(C_6H_7O_2)O_3(NO_2)_3$, it should contain 14.14 percent of nitrogen, but if it be $C_{24}H_{29}O_{20}(NO_2)_{11}$, it should contain 13.47 percent.

DETERMINATION OF ASH.

This may be done by melting some pure paraffin in a weighed platinum crucible, by gentle heat, adding a known weight of the sample and igniting from above. The mixture burns gently, and, when all is consumed, the crucible is ignited, cooled and weighed again. The increased weight gives the ash.

Or we may dissolve the sample in pure concentrated nitric acid in a weighed platinum dish, evaporate the solution carefully to dryness, ignite the residue and weigh again.

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DETERMINATION OF MOISTURE.

This may be done by drying in an oven at 40° C for twelve hours and then in a dessicator over sulphuric acid to constant weight.

DETERMINATION OF ALKALINE SUBSTANCES.

For certain purposes it is desirable to know the amount of calcium and sodium compounds present in the finished gun-cotton. For this test five (5) grams of the air-dry gun-cotton are taken from the center of the disks or blocks, rubbed up finely and extracted by means of 100 $cm.^{-3}$ of standard hydrochloric acid diluted with about twice its volume of water. The acid and gun-cotton are allowed to digest together for a short time, the liquid is decanted and the gun-cotton washed, either by decantation, or upon a filter, until the washings exhibit no acid reaction. The washings are added to the decanted liquid, and 100 $cm.^{-3}$ of standard sodium carbonate solution is poured in. Then the amount of sodium carbonate neutralized is determined by titrating with standard acid solution and an indicator. The unneutralized sodium carbonate is the measure of the alkalies in the gun-cotton.

The standard sodium carbonate solution should contain three (3) grams of salt in 100 $cm.^{-3}$, and the standard solutions are so arranged that equal volumes neutralize each other.

PREPARATION OF FINISHED SAMPLES FOR HEAT AND SOLUBILITY TESTS.

Split the disk or block and then, by gentle scraping or rasping, remove about forty (40) grams of the gun-cotton from the center of the mass. Place this in a liter flask, pour upon it a half liter of distilled water at a temperature of 39° C, cork the flask and shake it vigorously for

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two or three minutes. Then pour the contents on a piece of muslin, which is wrapped up and squeezed in the hand press. The gun-cotton is washed three times more with water in the way above described, being squeezed after each washing, when it is ready for the application of the tests.

SERVICE METHODS OF INSPECTION.

Inspection of wet gun-cotton.
Weekly inspection of dry primers.
Monthly inspection of dry primers.

Description of the methods to be pursued will be found in "Gun-cotton Torpedo Instructions," p. 39; 1888.

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LECTURE IX.

NITRO-GLYCERINE.

The discovery of the fact that cotton when immersed in nitric, or in a mixture of nitric and sulphuric acids, was converted into a highly explosive substance gave rise to a warm controversy among the chemists of the day as to the nature of the change which had taken place, one party holding that the change was a true chemical one and was due to the substitution of certain of the components of the nitric acid for certain components of the cotton resulting in the formation of a new compound substance, while the other party held that it was physically impossible that so delicate a material as cotton fibre could change its elements without a more obvious change of structure, and that the change was simply a physical one due to the absorption of the nitric acid in the pores of the cotton, just as nitre is absorbed by paper in the manufacture of touch paper, and that thus the inflammability of the substance was increased. It is obvious that with such a difference of views prevailing the true one could only be established by experimental evidence, and hence the promulgation of these views led to many experiments being made upon a large number of substances which were analogous in their chemical characters to cotton.

Pelouze, the French chemist, was one of the more

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active advocates of the theory of exchange, and, among other experiments, he suggested to his pupil, Sobrero, that he should study the effects of nitric acid on glycerine, because, as the latter was chemically analogous to cotton, it was probable that, if the change was a chemical one, an explosive body would be formed, and it was obvious that, if an explosive body was formed, it must be due to replacement, for it was exceedingly unlikely that a liquid like glycerine could absorb and retain in its pores, by mere physical force, a liquid like nitric acid. Sobrero made the experiment and discovered nitro-glycerine, which announced its birth by a violent explosion which shattered the windows of the laboratory and wrecked the apparatus.

The great power which this explosive exhibited, and the apparent readiness with which it exploded, conspired to make chemists somewhat reluctant to pursue the investigation of the character and properties of this substance, and so, although Sobrero made his discovery in 1846, little was done with it until the Crimean war, when it was asserted that Professor Jacobi had manufactured the explosive in quantities for the Russian government, and that its reputed presence deterred the English from entering the harbor of Cronstadt, though, during this time, it was employed in very small quantities as a medicinal agent under the name of *glonoine*.

The practical use of the substance as an explosive agent is due to Alfred Nobel, a Swedish engineer, whose name is indissolubly connected with and pre-eminent in the history of nitro-glycerine explosives, and who, about 1860, invented a process for its rapid manufacture which he patented under the name of *detonating oil* or *Nobel's Sprengœl*, and between this and 1863 established factories on the continent of Europe for its manufacture on a com-

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mercial scale. At this time Nobel used the same means for explodimg the substance as were employed for firing gunpowder, with the addition, sometimes, of a priming charge of gunpowder, but it was found that, even when confined, the nitro-glycerine was but partially exploded. In 1863, however, he discovered that it could not only be exploded with certainty by means of a cap containing mercury fulminate, but that the power developed was enormously greater than could be obtained for it by any other means. The discovery of this fact marks not only an epoch in the history of nitro-glycerine but in that of all explosives, since it revealed to us the method of inducing explosion by detonation.

Great expectations were aroused by the announcement that the enormous force stored up in nitro-glycerine was completely under control and could be used at will for doing useful work, and it found its way to the scene of mining operations in many parts of the world. Scarcely a year elapsed after Nobel had secured his patents in Norway before the substance made its appearance in this country, but the fact of its presence was announced in a very startling manner.

One of the guests of the Wyoming Hotel, in New York, wishing to polish his boots drew from under the counter a small box upon which to rest his foot, the box having been used for this purpose for sometime. While busy with his work he noticed a reddish vapor coming from the box, and he called the clerk's attention to it. The latter took the box, carried it to the door and threw it into the street, when it instantly exploded, and so violently that the pavement was torn up, the passers by were thrown down, and the windows in every house within 100 yards of the entrance to the hotel were shattered. Great excitement was created by the explosion,

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and great interest was exerted to learn the character of the agent which caused this disaster. On inquiry it was ascertained that some weeks previously a guest who had recently come from Germany, being pressed for means, left the box as security for his board, stating that it contained Glonoin Oil, a new material which had been used, with great success in Germany, for blasting. Glonoin oil was but another name for nitro-glycerine.

This accident was not long after followed by one at Aspinwall, another at Wells, Fargo & Co.'s office in San Francisco, another at the factory at Stockholm, and still others, which were so inexplicable and disastrous as to lead to public reprobation of this dangerous and, to most people, mysterious and diabolical compound, and many governments, among them Sweden, Belgium and England, totally prohibited its use, so that the effort to introduce it seemed destined to failure. But it was observed that these accidental explosions were exceptional, and that in repeated instances nitro-glycerine had been transported long distances, both by sea and by land, and had been stored for considerable periods of time without undergoing explosion, and, as the agent was too valuable a one to be abandoned if its safety could be in any way ensured, several chemists were encouraged to further investigate its properties and to seek to discover and remove the causes which had operated to produce these premature explosions.

Notable among these investigators were the American chemists, Mowbray and Hill, and through their efforts the difficulties attending the production of a pure and stable substance have been surmounted, so that for many years past nitro-glycerine has been manufactured, stored, transported and used with comparative safety and with less attendant danger than surrounds gunpowder.

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The manufacture of nitro-glycerine is based upon the reaction which takes place when glycerine is brought in contact with nitric acid, and which may be represented by

$$C_3H_5O_3H_3 + 3HONO_2 = C_3H_5O_3(NO_2)_3,$$

in which one molecule of glycerine being acted upon by three molecules of nitric acid yields one molecule of tri-nitro-glycerine, (or better, glyceryl trinitrate), and three molecules of water. Three of the atoms of hydrogen in the glycerine being replaced by the three atoms of nitryl (NO_2) in the three molecules of nitric acid.

It is believed to be possible to produce three different nitro-glycerines. By replacing one atom of hydrogen in the glycerine by one atom of nitryl the mono-nitro-glycerine is formed, having the formula $C_3H_5O_3(NO_2)_2H$. By replacing two of the atoms of hydrogen by two of nitryl the di-nitro-glycerine is produced, having the formula $C_3H_5O_3(NO)_2H_2$. By replacing the three atoms, we get the tri-nitro-glycerine given in the reaction above.

It is believed also that the tri-nitro-glycerine is the only one of these compounds which is stable and that many of the accidents which have been caused by nitro-glycerine have been due to the presence of these other compounds in the tri-nitro-glycerine.

To produce pure nitro-glycerine it is necessary that we should use the purest, most concentrated glycerine and purest, strongest nitric acid. The presence of any fatty impurities in the glycerine gives rise to the formation of unstable bodies which cause the decomposition and spontaneous explosion of the nitro-glycerine, while the presence of iron, alumina or chlorine seriously interferes with the separation of the nitro-glycerine. It has been difficult to obtain anhydrous glycerine and anhydrous nitric acid, hence it is the custom to use the most

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concentrated articles to be obtained and to mix with them some substance which will absorb the water present and thus render them anhydrous. The importance of using an exsiccating substance is further shown, if we refer to the reaction, by the fact that water is one of the products of the reaction, and hence, if we were to start with anhydrous glycerine and nitric acid, after a portion of the glycerine has been converted, the water formed will have so diluted the remainder that there is danger of the lower nitric esters being formed.

Concentrated sulphuric acid is used as the exsiccating substance, and it is added in sufficient quantity to combine not only with the water contained in the original substances but also with all the water formed during the operation. But in using the sulphuric acid another element of danger is introduced. The sulphuric acid removes the water by entering into chemical combination with it, a hydrate of sulphuric acid being formed, and this combination is attended with the development of heat. If the temperature is raised somewhat there is danger of the nitro-glycerine being exploded, or if an explosion does not result, the glycerine will be wasted by being converted into oxalic acid and other products, which may render the nitro-glycerine unstable. Hence it is necessary to keep the mixture cool while the conversion is taking place, and in the process of manufacture this is effected by means to be described.

I have thus attempted to state as briefly as possible the rationale of the operations in the manufacture of nitro-glycerine, and I will now describe some of the processes employed.

Sobrero, the discoverer of nitro-glycerine, proposed the following process for its manufacture: one-half oz. of anhydrous glycerine is poured with constant stirring

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into a mixture of two ozs. of concentrated sulphuric acid and one oz. of fuming nitric acid of Sp. Gr. 1.52, the temperature of the mixture being kept below 24° C by external cooling with ice, and as the oily drops begin to form on the surface, the mixture is poured with constant stirring into fifty ozs. of cold water. Nitro-glycerine then separates and may be purified by washing and drying in small portions, in a vapor bath.*

De Vrij's process differs from the above only in the the proportion of the acid used and in the fact that the sulphuric acid was added after the mixture of the glycerine with the nitric acid had been effected.

The Mowbray process, as used at North Adams and at the Torpedo Station in a form much improved by Hill, is as follows:

The glycerine employed must be free from lime, iron, alumina, chlorides, fatty acids, and glucose or other adulterant, and must have a Sp. Gr. of 1.26.

The nitric acid must be strong, having a specific gravity of not less than 1.49 to 1.51 (48°–49° B), and this strength should be real and not factitious as is often the case with acids nominally testing 50°–52° Baume. Nitric acid of this strength must be specially prepared for the purpose. This is done by careful distillation from sodium nitrate (Chili saltpetre) and sulphuric acid (oil of vitrol). Another and perhaps a better method is to distill from a mixture of ordinary commercial nitric acid and sulphuric acid in glass retorts. Stronger nitric acid can thus be made, but with more trouble and expense.

Before it is used the nitric acid is mixed with twice its weight of strong sulphuric acid, Sp. Gr. 1.845, the acids being now readily purchased in the market mixed in these proportions.

*Liebe, *Arch. Pharm.* 103, *158;* 104, *282.*

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The sulphuric and nitric acids, mixed in their proper proportions, are placed in a large stoneware receiver, from which the mixture can be drawn as it is required.

The operation may be conveniently divided into two parts:

1st. The conversion of glycerine into nitro-glycerine.

2d. The separation and washing of the nitro-glycerine.

Conversion of Glycerine into Nitro-Glycerine: The apparatus used for this purpose at the Station is shown on Plate 1. An elevation, section and plan are given, the lettering being the same in each.

A, A, A, A, A, A, are wooden troughs placed around the brick chimney D, D. In these troughs are earthenware pitchers, *a*, *a*, *a*, *a*,. . *a*, which contain the acid mixture. On the shelf B, above the pitchers, are bottles, *b*, *b*, *b*,. . *b*, which contain the glycerine. The bottles are loosely closed by wooden stoppers with broad rounded tops. The rubber tubes, *c*, *c*, *c*, *c*, which reach to the bottom of the bottles and carry small glass jets at their outer ends, pass loosely through holes in these stoppers. Conical wooden plugs, *e*, *e*, *e*, *e*, are placed in the holes through the stoppers alongside the rubber tubes.

The steam pipe G passes along the shelves B, B, just behind the glycerine bottles. The air-main F passes under the shelf B, and carries on its under side a number of short pipes or jets (two for each pitcher) to which are attached the rubber tubes, *d*, *d*, *d*, *d*, which hang over the pitchers. Glass tubes long enough to extend to the bottom of the acid pitchers are inserted in these rubber tubes. In the elevation these tubes are out of the pitchers, but in the section they are in place, as if in use.

The troughs are made tight to hold the ice water with which the pitchers are surrounded. Partitions, with openings at the bottoms, cut off the corners of the

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troughs forming the clear spaces, *f*, *f*, *f*, *f*. These water spaces are convenient as affording opportunities for quickly emptying a pitcher into water if it becomes necessary. A pipe is placed in one corner of each trough through which the water may be drawn off into the escape E, when the operation is finished. The pitchers stand on narrow strips, which raise them off the bottom about two inches, thus giving the cold water free access all about them, and when in position they are well under the overhanging hoods, C_1, C_2. These hoods are flat wooden boxes, wide at the bottoms and drawn in at the tops, where they fit against openings in the chimney D, D. In the lower part of the chimney, on the floor below, is placed a grate and fire door (not shown in drawing).

Each pitcher receives 18 to 20 lbs. of the acid mixture (according to the strength of the latter). All are then set in place in the troughs, covered with glass plates, surrounded with ice and water, and allowed to stand until completely cooled. Two lbs. of glycerine are put into each bottle.

When the acid in the pitchers has fallen to the temperature of the surrounding ice water, the covers are removed from the pitchers, and the air-tubes passed through holes in the hoods down into them. A strong current of air is forced through these air-tubes by means of a pump driven by steam, and this current of air keeps the contents of the pitchers in continual agitation. The air for the pump is drawn through sulphuric acid to render it perfectly dry, and just before it enters the air-main over the troughs it is thoroughly cooled.* The cooling

*The pump draws its air from the top of a large tight box; in the bottom of the box is placed a leaden pan containing sulphuric acid (oil of vitrol), in which a flat spiral of lead pipe is immersed. The inner end of the pipe is closed, and the outer end rises out of the acid and passes through the side of the box into the open air. A great number of small holes are bored in the spiral. As fast as the air is drawn from the upper part of the box the outside air enters through the pipe, bubbling up through the acid. Drying the air is not absolutely necessary, but since it can be so readily accomplished it is better to do it. Cooling does not entirely remove moisture, and the quantity of air forced through the pitchers is large.

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arrangment is made of 10 coils of small tin pipe, which are surrounded by ice (or better, ice and salt).* These coils are so arranged as to give an extensive cooling surface without impeding the current.

As soon as the air-current has been turned on the flow of glycerine is begun. Each rubber tube *c* is a siphon, which is started by suction through a glass tube inserted in the outer end. As soon as the glycerine runs freely, the suction tube is withdrawn and a fine-pointed glass jet put in its place. The glycerine runs from this jet in a fine stream directly into the pitcher under it. In cold weather the glycerine may become too thick to flow easily. To overcome this the bottles of glycerine are warmed by passing steam through the pipe behind them until the glycerine is sufficiently thin.

The glycerine dropping into the acid mixture is rapidly acted on and converted into nitro-glycerine. The reaction is accompanied by a considerable evolution of heat. This heat must be removed, for if the temperature be allowed to rise too high the glycerine is not converted into nitro-glycerine, but is oxidized or burned, with formation of other substances. The limits of temperature are very narrow. Starting at 72° F, the temperature must not be allowed to exceed 80° F; above 80° F there is great danger of "firing" taking place. The liquid in the pitchers is kept cold by surrounding them with ice-cold water and by the stream of cold air passing into the acid. The most important work of the air current is to keep the acid mixture in constant agitation. In this way the heat generated is quickly diffused through the whole, preventing any sudden local rise of temperature.

The glycerine is much lighter than the acid mixture,

*This is much preferable to allowing the air to come in direct contact with the ice.

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and would be apt to collect in little pools above it, and when these were broken up and a quantity of glycerine suddenly brought into contact with the acid, the action would be so rapid that it could not be controlled.

While the glycerine is running into the pitchers, observations with the thermometer are constantly made of the temperature attained in them. If the temperature in a pitcher is found to be rising too rapidly and to be approaching the higher limit, the glycerine is evidently running in too fast, and its flow must be checked, which is done by pressing down the conical wooden plug in the stopper of the glycerine bottle. This plug passes through the same opening as the rubber glycerine tube; therefore, when it is pressed down, it compresses the latter so that less liquid can pass through. If the temperature is too high or continues to rise, the plug is forced hard down, closing the glycerine tube altogether. The flow of glycerine being checked or stopped, the pitcher rapidly cools down again. As soon as the thermometer shows this to be the case, the plug is loosened and the flow again set up. Constant care is therefore necessary, but the operation is a simple one, easily learned and performed by ordinary workmen.

If the limit of temperature is exceeded "firing" takes place, indicated by the copious evolution of red, nitrous fumes, and in extreme cases by flame. Usually when this occurs it is easily controlled by stopping the glycerine stream and vigorously stirring the contents of the pitcher, but if it is violent the pitcher must be emptied into water as quickly as possible.

During the operation of conversion, acid and irritating fumes are given off in large quantities, greatly to the injury of those compelled to breathe them. In the apparatus at the Station these are entirely removed through

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the hoods and chimney. A fire in the grate at the bottom of the chimney causes a powerful draught in the hoods, which overhang the pitchers, drawing upwards all the fumes and discharging them into the open air. Generally a small fire at first is sufficient, and often no fire is necessary. This arrangement for removing the fumes has proved to be of great advantage, not only to the health of the workmen, but also to the operation itself, since they can attend more thoroughly to their work when not inconvenienced by the fumes. The hexagonal shape of the apparatus is of course not important, but happened to be convenient for the building in which it is placed and the number of pitchers to be used. In larger establishments the same principle can easily be applied in other ways.

Separation and Washing of the Nitro-Glycerine.—As soon as all the glycerine has been run into the pitchers the conversion is complete, but the nitro-glycerine has to be separated from the large quantity of acid still remaining. This acid is almost entirely sulphuric acid, very nearly all the nitric acid having been used up in the reaction. The nitro-glycerine is partly in solution and partly suspended in the heavy acid liquid. On diluting the acid with water, the portion in solution is precipitated, and as nitro-glycerine is a much heavier liquid than the diluted acid the whole of it settles to the bottom.

A sketch illustrating the separating and washing apparatus is given on Plate II. The wooden tub A is sunk in the floor of the converting room. It is filled about three-quarters with water, and has a cover with a square opening, in which a leaden strainer is placed. By means of a rubber hose connected with an air pipe, a current of air for agitating the water in it is led to the bottom of the tub. The pitchers are taken from the converting appara-

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tus, and their contents poured through the strainer into the tub. The acid liquid descends in fine streams and is quickly diffused through the whole body of water.

When all the pitchers have been emptied the air-pipe is withdrawn, and a short time allowed for settling. The heavy nitro-glycerine collects at the bottom of the tub, so that the lighter acid water may be drawn off from above it. A wooden cock, *b*, is put into the side of the tub, a short distance from the bottom, but above the level of the nitro-glycerine. Through this, the supernatant acid liquid is run off and led by a rubber hose into the drain *g*. The tub is placed in an inclined position, and in the lowest part of the bottom is another wooden stop-cock b_2. Through this the nitro-glycerine is drawn in small quantities into the washing-tub B. The washing-tub is of wood, lined with lead, and is supported by trunnions in the wooden frame E. The trunnions are placed just above the middle, so that the tub will stand upright and yet can be easily turned or inverted. The pipes *d* and *e*, provided with valves are directly over the washing-tub and within the reach of the operator standing by the tub. One is a water pipe and there is attached to it a short piece of hose. The other is connected with the air main, and has a piece of hose long enough to reach to the bottom of the washing-tub.

A portion of the nitro-glycerine in the large tub A, having been drawn into the tub B, the air-hose is put in and a stream of water turned on. The air-current causes strong ebullition, raising and spreading the nitro-glycerine through the water. As soon as this tub is full the water is turned off and the air-hose removed. The nitro-glycerine rapidly settles to the bottom of the tub, so that in a few minutes the water above it may be poured off by turning the tub on its trunnions.

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This operation is repeated until the nitro-glycerine is thoroughly washed, when it is poured into a copper pail, and a new portion taken from the large tub.*

When the wash water is decanted from B, it falls first into the tub C. As soon as this tub fills, the water runs off through the large lead pipe *f*, which descends nearly to the bottom of *c*, into the tight, open drain *g*. In this tub any nitro-glycerine which may have floated or been accidentally poured off has an opportunity to settle, and is saved. The building in which nitro-glycerine is made at the Station, is situated close to the shore, and the tight drain, *g*, extends below high-water mark.

When all the nitro-glycerine has been sufficiently washed it is poured into earthen jars, and allowed to stand, covered with water, until it "clears," when it is ready for use.

The time required for making a run of nitro-glycerine is about five hours, not including the time required for cooling the pitchers, which will of course be different at different seasons. The quantity made in this apparatus, when all the pitchers (24) are in use, is about 80 lbs.

This method of making nitro-glycerine is a convenient one from the simplicity of the apparatus, and has been found serviceable for the occasional requirements of the Station. But for steady work on a large scale it is not as desirable as other methods of operating. The handling of small quantities of material takes much time and labor, while the reaction goes on more steadily and regularly with larger masses of material. The simplest, and a very effective method, is to use a large amount of the mixed acid (2000 to 3000 lbs.) in a large leaden or iron

*Very thorough washing can be obtained by this method. Nitro-glycerine is a heavy, oily liquid, so that any ordinary washing fails to remove the acid contained in it. The powerful stream of air, however, breaks up the heavy oil into small globules, which are thrown up into the water above, so that there is a good opportunity for the washing action.

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tub, containing also coils of pipe through which cold water is forced; this tub is set within another of wood, and the annular space between is traversed by cold water; agitation of the acid is brought about by agitators driven by power (in some cases the agitators are driven by hand, but this is very objectionable). The glycerine is run in through an opening in the cover of the tub and distributed so as to fall upon the acid in a number of fine streams. The temperature is observed by a thermometer passing through the cover. When the desired amount of glycerine has been run in, the contents of the tub are drawn off into water and the nitro-glycerine separated.

In another form of apparatus a leaden tank is placed within a wooden one, so that water can be passed between them; in the tank a hollow shaft revolves about a horizontal axis, carrying paddles for a portion of its length, and for the remainder a cylinder, so that cold water may be led through the shaft and cylinder. The glycerine falls upon the surface of the revolving cylinder and is thus conveyed into the acid, which is agitated by the paddles.

Nobel's apparatus consisted of a vertical leaden cylinder placed inside a wooden cylinder. Cold water circulates between the two, and also through lead worms coiled up inside the lead cylinder. A double pipe, formed like an injector or gas blowpipe, leads vertically down to the bottom of the cylinder, the outer pipe carrying the glycerine, and the inner compressed air. A charge of acid is placed in the cylinder and the glycerine is injected into it by the compressed air, which also effects a very rapid and intimate mixing of the liquids.

At the Ardeer works of the Nobel's Explosives Co., a mixture of 1.2 tons of nitric acid (Sp. Gr. 1.5) with two tons of sulphuric acid (Sp. Gr. 1.84) is cooled down and run into the cooled lead tanks, and 7.5 cwts. of gly-

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cerine (Sp. Gr. 1.26) are injected in the form of a fine spray, the temperature being carefully watched and never allowed to exceed the danger limit. The completion of this nitrating process is indicated by the fall of the thermometer, owing to the cessation of the chemical action, and when the temperature has fallen to a certain point, the mixture of acids and nitro-glycerine is run off into another tank, where, by virtue of the different specific gravities, the nitro-glycerine separates in a short time and floats on the top of the acids, when it is drawn off and washed to purification.

The process of Boutmy and Faucher,* which is employed by the French Government at their works at Vonges, differs in principle from any of those described. In this process two mixtures are first prepared, one a mixture of nitric and sulphuric acids in equal proportions, the other a mixture of one part of glycerine to 3.2 parts of sulphuric acid. These are then thoroughly cooled, and they are then mixed together in the proportion of 5.6 parts of the nitric-sulphuric mixture to 4.2 parts of the sulpho-glyceric mixture. The whole is placed in an earthen pot, surrounded only by the atmosphere, and the operation is left to take place, which it does quietly, the nitro-glycerine separating as formed and rising to the surface of the liquid mass, from which it is eventually skimmed off, washed and purified.

The theory of this operation is that the glycerine and sulphuric acid form the glycerol-sulphuric acid,

$$C_3H_5 \begin{cases} (OH)_2 \\ O.SO_3H \end{cases}$$

and that this reacts with the nitric acid as follows:

$$C_3H_5 \begin{cases} (OH_2) \\ O.SO_3H \end{cases} + 3HNO_3 = C_3H_5O_3(NO_2)_3 + 2H_2O + H_2SO_4$$

*For a fuller description with drawings, see *Proc. Nav. Inst.* 5, 15; 1879.

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It is claimed for this process that it is is simple in execution, requires but little apparatus, is safe and gives a large yield. The claim for safety is questioned on the ground that the nitro-glycerine remains for a dangerously long time in contact with the acids, and the explosion at Pembrey Burrows, in 1883, where this process was used, is cited in support of this criticism. It may be replied that it is now the custom at the factories, where the other processes are employed, to allow the nitro-glycerine and acids to remain in contact for a long time, until the nitro-glycerine separates completely from the acids, so that by skimming, the acids may be recovered undiluted and be reworked, and that the opertion is not considered extra-hazardous, while, besides, Dr. Dupre′ found that very impure glycerine and acid had been used at Pembrey Burrows at the time of the explosion, and this was sufficient to account for its origin.

The object of separation by "skimming" is to recover the unconverted acids and thereby reduce the cost of manufacture. W. Poetsch* describes the method he employs as follows: On heating the waste acids, consisting of sulphuric and nitric acids and organic nitro-compounds, at 105°, decomposition of the nitro-compounds ensues, oxidation to carbon dioxide taking place at the expense of the nitric acid which is present. During the reaction enough heat is liberated to volatilize the remaining portion of undecomposed nitric acid and the lower oxides of nitrogen produced, pure sulphuric acid being left in the residue. Poetsch uses a closed vessel of stone or lead, having a perforated false bottom 50 cm. above the bottom. The upper space is filled with stones or broken stoneware, and heated by hot air. The waste acid is in-

*Dingl. polyt. J. 255, 216.

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troduced in a thin stream through a funnel fitted into the cover of the vessel, and, passing over the hot stones, is decomposed. The nitrogenous vapors are led through an earthenware pipe to a cooling worm, and collected in Wolff's bottles, air being introduced to oxidize the gases to nitric acid. The denitrated sulphuric acid then flows through the perforated bottom, and is run into receiving tanks.

From the equation we find that one part of glycerine should yield 2.46 parts of nitro-glycerine, but this is never realized in practice. The proportion of nitro-glycerine obtained is dependent almost entirely upon the acid used. If the glycerine is weak the product will fall off, but the small difference in strength of glycerine ordinarily found exercises little effect. If the acids are weak, however, the product is markedly less. This does not depend to any extent upon the method or form of apparatus operated, but only upon the acid taken. Weak acids will carry smaller quantities of glycerine and give lower proportional products than strong ones; consequently statements of relative products obtained are of comparatively little value unless accompanied by a statement of the kind of acid employed and the relative amount of glycerine treated. At Vonges they obtained 1.8, while the Ardeer works get 2 parts, the loss being accounted for by the supposition that other compounds are formed which are carried away with the acids. In this country we obtain rather more than two parts, using one part of glycerine to from 7.5 to 8 parts of mixed acids, and with care in the preparation of materials 2.2 parts can be obtained.

In all processes for making nitro-glycerine the greatest care must be taken to prevent any accidental mixture of water with the charge in the converter. A very little

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water shows itself by the greater trouble and slowness experienced in running and in the falling off of the product. If more water enters, the heat will be greater than can be carried away by the usual means of cooling, and the charge is "fired." Usually this means only an active decomposition accompanied by clouds of nitrous vapors. Slight "fires" may be stopped by vigorous agitation, but if the firing is persistent, the contents of the tub should be run off as rapidly as possible. A constant agitation of the liquid should be kept up during drawing off to prevent separation of the nitro-glycerine.

When mixing the glycerine in the converter the operation is slowly performed in order to keep the temperature down, but, if the temperature is within the limit, the mixing should be performed as rapidly as possible and the nitro-glycerine removed from the sphere of action. Rapidity of working is largely dependent upon the quality of acids used, since the heat evolved is least when the strongest acid is used. In general with highly concentrated acid, not only is the product proportionally increased, but the reaction also goes on more uniformly and is more readily controlled.

At ordinary temperatures nitro-glycerine is an oily liquid having a specific gravity of 1.6. Freshly made, by the Station method, it is creamy-white and opaque; but becomes transparent ("clears") and colorless, or nearly so, on standing for a time, which is dependent on the temperature. When produced by "skimming" it is transparent, but it is often found in commerce to have a yellow or brownish-yellow color. Although very slightly soluble in it, it does not mix with and is unaffected by cold water. It has a sweet pungent, aromatic taste, but is an active poison, so that mere contact with it will induce in most persons a violent sickness and an especially painful form

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of headache, but those constantly employed about it, as a rule, soon lose their susceptibility to its action. Strong black coffee is recommended as an antidote. It is used in minute doses as a medicine, or rather as a palliative, in cases of *angina pectoris*.

Nitro-glycerine is soluble in methyl ethyl and amyl alcohols, in benzene, in carbon disulphide, in all proportions in ether, chloroform, glacial acctic acid and phenol, and sparingly in glycerine. It is rapidly decomposed by alkaline sulphides with the separation of sulphur, and slowly decomposed by an alcoholic solution of potassium hydroxide, by ammonia, alkaline carbonates, hydrogen-sodium phosphate, hot water, ferrous chloride, hydrogen chloride and sulphuric acid (1 : 10), though, according to Hay,* concentrated sulphuric acid has no action upon it. It presence may be detected by a solution of aniline in concentrated sulphuric acid which yields a purple color with nitro-glycerine that changes to green on the addition of water. The stability test for nitro-glycerine, and explosives of which it forms a part, is the same as that used for gun-cotton, but the time required is but ten minutes.

Freshly made, opaque, nitro-glycerine freezes at from — 3° to — 5° F, while the transparent or "cleared" nitro-glycerine freezes at from 39° to 40° F, in both cases freezing to a white crystalline mass. Once frozen it remains in this condition, even when exposed for some time to a temperature sensibly above its freezing point. When frozen it may be conveniently and safely thawed by placing the vessel containing it inside another containing water not hotter than 100° F, but these precautions should be strictly observed, as most of the accidents which have occurred with nitro-glycerine, and explosives

*Trans. Roy. Soc. Edin. 32, 67.

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of which it forms a part, have resulted from foolish and criminally careless attempts to thaw the frozen material by other means. Frozen explosives should never be put into the vessel containing the water, or brought into contact with any heated surface, except as directed above.

Pure nitro-glycerine does not spontaneously decompose at any ordinary temperature, but if it contains free acid, decomposition is apt to occur, and it is therefore very important that all acid should be removed by washing with water and alkaline solutions. Quantities of nitro-glycerine have been kept in the magazines at this Station for years, without special precautions having been taken to protect them, and yet they have remained entirely unaltered, nor has any case yet been noticed of the spontaneous decomposition of the properly made and purified substance. According to A. Brull,* when, owing to the presence of free acid, decomposition does set in, it proceeds in a slow and tranquil manner, disengaging nitrous vapors, which color the liquid green, then developing nitrogen and carbon dioxides and crystals of oxalic acid, until, after some months, the entire mass is transformed into a greenish, gelatinous body composed of oxalic acid, water and ammonia. Sometimes, if the temperature is high, as when heated by the sun, the decomposition is more active, but it by no means always leads to an explosion, though this must depend somewhat upon the quantity involved.

Pure nitro-glycerine is not sensitive to friction or moderate percussion, except when pinched between metallic surfaces. If placed upon an anvil and struck with a hammer, only the particle struck, as a rule, explodes, scattering the remainder. A quantity of it has been thrown up by means of a rocket to a height of 1000

*Etudes sur la nitro-glycerine, Paris, 1875.

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feet, from which it fell without being exploded on impact. When, however, in a state of decomposition, it is exceedingly sensitive and explodes violently when struck, even if unconfined. It must be noted that if completely confined, the effect of a blow on pure nitro-glycerine may produce explosion, since, from its liquid form, it is nearly incompressible. In the case cited above local explosion occurs only because the hammer is lifted, and the rest of the explosive is blown away, but if it was so confined that there was no escape for the effect of the explosion of the particle first struck, the whole mass would probably be fired.

If nitro-glycerine is freely exposed to flame it burns with a brilliant flame and without explosion. If a drop of nitro-glycerine be placed on a metal plate and slowly heated up, the nitro-glycerine may be completely vaporized without explosion, or if the plate be first heated to incandesence and the drop then placed upon it, the drop will assume the spheroidal condition and eventually volatilize without explosion, but if the hot plate be just below incandesence, so that the nitro-glycerine can come in contact with it, the drop explodes with a violent report. The firing point of nitro-glycerine is about 180° C (356° F), but it begins to decompose under the influence of heat at a somewhat lower temperature.

Nitro-glycerine is fired by means of detonators or blasting caps containing mercury fulminate, it being more readily detonated by this means than gun-cotton is. It is essential for success that the detonator should be immersed in the liquid so as to be in direct contact with it, but when the caps are fired by means of a running fuse care should be taken that the fuse does not touch the nitro-glycerine, as the latter may be set on fire before the cap explodes, and an incomplete explosion, which would

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produce poisonous fumes and cause a loss of energy, might then result. When fired by a gun-powder fuse only, the action is very uncertain, for sometimes the nitro-glycerine is exploded and sometimes not, and even when it is exploded by this means, the force developed is much less than when it is detonated by means of a fulminate. It may be detonated, even when frozen, by means of a heavy charge of fulminate, but the action is not certain. Its insensitiveness when in the frozen condition is shown by the fact that 1600 pounds of the liquid exploded in a magazine which contained also 600 pounds of the frozen, and that the latter was broken up and scattered in every direction without being exploded.

Nitro-glycerine may be conveniently stored in large earthen crocks, which should be placed in copper buckets to catch the nitro-glycerine, if by any means the crocks should be broken. There should be a layer of water above the nitro-glycerine, and this should be tested with litmus paper as often as once a month to determine if any acidity is being developed in the explosive. If a slight reaction is detected the explosive should be thoroughly washed as described. If the acid reaction is strong, and especially if any green color is developed in the explosive, it should be destroyed, the best means for doing so being by exploding it in a safe place.

The liquid form is very inconvenient for transportation owing to the danger of leakage; it is therefore advisable to freeze the nitro-glycerine and carry it in the frozen state, as it is then perfectly safe. For this purpose it should be put in strong tin cans holding about 45 or 50 pounds, each can being paraffined on the inside and provided with a tin tube passing vertically through its centre, so that freezing or thawing may be more easily accomplished. All vessels in which nitro-glycerine has been kept should

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be destroyed when not wanted for the same use, as the nitro-glycerine cannot be easily washed off. Should any nitro-glycerine be accidentally spilled it can be safely destroyed by means of a solution of an alkaline sulphide.

Nitro-glycerine is one of the most powerful explosives in use. In difficult blasting, where very violent effects are required, it surpasses all others. In spite of the many accidents that have occurred with it, it has been found to be so valuable that its use has steadily and largely increased. Its liquid form is a disadvantage, except under favorable circumstances, such as when made at the place where it is to be employed. It, however, forms the essential ingredient in a number of solid mixtures, which will be considered later. When used in blasting or similar work it is usually put in tin cans or cartridge cases. A very good case may be made for it by rolling up stout brown paper into a cylinder of the desired diameter, glueing it, and fastening into one end a cork by choking with fine wire. When dry the case is soaked in melted paraffine. The fuse wires should pass snugly through a cork which fits the open end. This cork may be firmly fixed in the case by means of small tacks. If the bore holes are water-tight it may be poured directly into them, but it is rarely safe to do this, as there is great danger that some of it will escape through seams in the rock and not be exploded, remaining to cause accident at a future time.

Since nitro-glycerine is so readily detonated it has the advantage of not requiring strong confinement. Even when freely exposed it will exert violent effects, such as breaking masses of rocks or blocks of iron. So, in blasting, it requires but little tamping. Loose sand or water is entirely sufficient.

The relative force of nitro-glycerine is not easily estimated, since the effect produced depends greatly on the

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attendant circumstances. Thus, a charge of nitro-glycerine in wet sand or any soft material will exercise but a slight effect, while the same charge will shatter many tons of the hardest rock. In the former case much more sand would be thrown out by a slower explosion, which would gradually move it, than by the sudden violent shock of the nitro-glycerine, which would only compress the material immediately about it. But in the hard rock the sudden explosion is much more effective than the same amount of force more slowly applied. Roughly speaking, it may be said that nitro-glycerine is eight times as powerful as gunpowder, weight for weight.

Nobel states that when nitro-glycerine is completely exploded it is resolved into carbon dioxide, water, nitrogen and oxygen, which may be expressed by the equation

$$4C_3H_5O_3(NO_2)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2,$$

from which we see that the *molugrams** yields

By Weight		and by Volume at 0° and 76 cm.		
132 grams	$22.32 \times 3.$	$= 66.96$	liters	CO_2
45 "	22.32×2.5	$= 55.80$	"	H_2O
42 "	22.32×1.5	$= 33.48$	"	N
8 "	$22.32 \times .25$	$= 5.58$	"	O
		161.82		

Berthelot† gives the heat of combustion, or calorific power of nitro-glycerine, as 356500 cal. Sarrau and Vieille have obtained 360500 cal. by direct experiment. We will use the lower of these two numbers for deter-

*I have coined this word to represent the molecular weight of a substance taken in grams. Supposing the substance to be in the state of a gas this weight has a constant volume, at 0° and 76 cm., of 22.32 liters. Its numerical value for nitro-glycerine is 227 grams.

†*Sur la force des matieres explosive* 2, *25;* 1883.

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mining the calorific intensity, while for the specific heats of the products, or $W_1S_1 + W_2S_2 +$ etc., we have

$$\begin{aligned} 132 \times .2169 &= 28.63 \\ 45 \times .4805 &= 21.63 \\ 42 \times .2438 &= 10.24 \\ 8 \times .2175 &= 1.74 \\ \text{Total,} \quad & 62.64 \end{aligned}$$

and $\frac{356500}{62.24} = 5728°$ is the calorific intensity,

$$\text{then } V' = \frac{161.82 \times 6001}{273} = 3557 \text{ liters,}$$

or one gram of nitro-glycerine will yield $\frac{3557}{227} = 15.7$ liters.

The density of nitro-glycerine being 1.6, one cubic centimeter will weigh 1.6 grams, and, therefore, one cubic centimeter will yield 25 liters of gas and, the volume remaining constant, it will exert a pressure of 25000 atmospheres, or 164 tons per square inch.

The velocity of propagation of the explosive wave, when the nitro-glycerine is enclosed in tubes of 3 mm. in diameter, is, according to Berthelot,* but from 1078 to 1386 meters per second, it being 2333 to 2753 meters for dynamite and 5200 to 6000 for compressed pulverulent gun-cotton. This is remarkable as the highly elastic, nearly incompressible liquid ought to be the better conductor.

Nitro-glycerine is now but little used in the free state. its principal use in this condition being for "shooting" oil wells, in order to free them from the paraffins with which they become clogged, or to shake the oil bearing sandstone, so as to increase the yield. The torpedoes used for

*Comptes rendus 100, 314; 1885.

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this purpose consist of tin shells from three to five inches in diameter, and from five to twenty feet in length. The shells are taken to the well empty, the longer ones being in sections which are put together as they are inserted in the well. After the shells are inserted they are filled with the explosive, closed with a tightly-fitting cover to which a strong percussion cap is attached, and lowered to the bottom of the well (which is often 1500 feet or more in depth) by means of a wire. A perforated iron weight is then strung on the wire, and when the torpedo is in place it is exploded by allowing the iron weight to drop from the surface and strike upon the cap.

An advantage which nitro-glycerine possesses over gun-powder for use in mining is that in the liquid state it may be poured directly into the bore-hole, and that it may readily and easily be tamped by pouring water upon it, thus avoiding the dangerous process of tamping by ramming, which has given rise to many accidents and caused the loss of many lives. It is obvious, however, that liquid nitro-glycerine can be used for this purpose only in holes which tend downwards, while in the operation of mining it is necessary to drive holes in every direction. This together with the fact already noticed that the liquid state made nitro-glycerine a difficult substance to store, transport and use with safety, impressed the manufacturers with the necessity for devising some means by which it could be converted into such a solid state that the dangers noted could be avoided, while its great power and susceptibility to detonation could still be availed of at will. How this has been accomplished will be shown in the next lecture.

It should be noted here, however, that a device employed by Nobel to render nitro-glycerine insensitive, until desired for use, was by adding 15 to 20 percent of

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methyl alcohol to it. The two liquids were perfectly miscible, and the mixture was completely insensible to blows and even to detonation. When desired for use 6 to 8 volumes of water were added, which precipitated the nitro-glycerine out unchanged. It can readily be seen, however, that this scheme was commercially impracticable.

Reference books, *Hill's Notes, Proc. Nav. Inst., Desortiaux, Berthelot, Cundill's Dict. of Explosives,* 1888.

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LECTURE X.

DYNAMITE—GUN-COTTON POWDERS—EXPLOSIVE GELATINE.

We have shown that the many objections to the liquid state urged Nobel to devise some means for changing it, but the prohibition which was issued against the use and transportation of nitro-glycerine, no doubt operated as a more powerful stimulus, as, in the existing state of things, it made his invention worthless and wiped out the capital invested in the plants designed for its production. After many efforts the defects of the liquid state were overcome, the dangers attendant on transportation and use were neutralized, and financial disaster was prevented by the invention of *dynamite*, which was perfected in 1866 and put up for sale about June, 1867.*

This body is described in his English patent† as follows: "This invention relates to the use of nitro-glycerine in an altered condition, which renders it far more practical and safe for use. This altered condition of the nitro-glycerine is effected by causing it to be absorbed in porous inexplosive substances, such as charcoal, silica, paper, or similar materials, whereby it is converted into a powder, which I call dynamite or Nobel's safety pow-

**Proc. Nav. Inst.* 14, *155;* 1888.
†*Spec.* No. 1345, 7, *5, 67.*

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der. By the absorption of the nitro-glycerine in some porous substance it acquires the property of being in a high degree insensible to shocks, and it can also be burned over fire without exploding."

It will be observed that the nitro-glycerine is not really converted by this means into a solid, but that it is only stored up in and conveyed in the solid, which sucks it up and retains it in its pores, just as it would any other liquid, through the force of capillarity. It is stated that this discovery was accidental, some nitro-glycerine having leaked from the cases, in which it was being transported, into the sawdust, in which the cases were packed, and having been absorbed and retained by the sawdust. It is highly probable that such an accident did occur, and that the observation of this occurrence, combined with a knowledge of the well-known action of porous and finely-divided solids towards liquids, suggested the application of the principle to the solution of this problem, and led to the carrying on of the experiments necessary to determine which solid was best fitted for the purpose; what the conditions were under which it could be depended upon to retain its liquid contents; and whether under these circumstances the nitro-glycerine contents could be detonated with ease and certainty and so as to produce a useful effect.

Among the many solids available, the substance known as *kieselguhr* was chosen as best fitted for this use, on account of its high absorptive power; the firmness with which it retained the liquid under considerable variations of temperature; its great chemical stability and entire inability to react with the nitro-glycerine; its abundance; and its cheapness.

Kieselguhr is a substance which is familiar to all under the names of "tripoli" or "rotten-stone", and is now

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sold in commerce as a polishing powder under various fanciful names. It was formerly supposed to be the debris of disintegrated rock, and much surprise was exhibited when Ehrenberg announced that tripoli was entirely composed of the inorganic remains of countless millions of extremely minute organic beings called infusoræ or diatoms, and when it was further discovered that deposits of this kind were quite numerous and were constantly in process of formation over widely extended areas. Enormous deposits of this infusorial or diatomaceous silica were formed during the Tertiary period, and one such may be traced from Herring's Bay in Maryland to and beyond Petersburg, Virginia; Richmond being built upon a deposit which is twenty feet in thickness. Naturally when found it is more or less contaminated with impurities, and so it is calcined to drive off water and organic matter, while more or less of the accompanying sand is sifted away. It also generally contains a little iron, which accounts for the red tinge often seen in dynamite made from it.

When in a pure and dry condition kieselguhr will take up three times its weight of nitro-glycerine, and will retain it even at the highest ordinary temperature. To produce this change we have simply to place the weighed quantity of kieselguhr in a non-porous vessel, such as one of lead or wood, and pour upon it the weighed quantity of nitro-glycerine, and mix for a short time with a paddle, when the liquid will completely disappear, and we shall have a plastic mass which is scarcely, if any, moist to the touch. A better method of mixing is by means of a wheel mill made of wood with ebonite surfaces. Of course the nitro-glycerine in the mass has not undergone any chemical change and so might, like the liquid, develop traces of acid during storage or exposure,

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hence a small amount of an alkaline carbonate, such as sodium carbonate, or a carbonate of an alkaline earth, such as magnesium carbonate, may be mixed with the mass to correct any acidity which may be developed. Such a mixture as this described constitutes the original dynamite No. 1, now known as kieselguhr dynamite No. 1.

Dynamite No. 1 is a granular substance having a pearl-gray to reddish color, a plastic consistency like that of brown sugar, and a density of 1.5 to 1.6. For use it is put up in stout paper cartridge cases, of convenient size, which are coated with paraffine to render them impermeable to moisture. This protection against the action of water is important, for water drives the nitro-glycerine out from the kieselguhr, and the neglect to provide against this action has in several instances led to accidents. Dynamite keeps as well as the nitro-glycerine from which it is made. It is safer because it avoids the liquid condition, while from its softness it will bear blows better. This was shown by experiments made by Nobel at Redhill, where a box containing 4 kilos of dynamite was thrown from a height of 20 meters on to the rocks below without causing explosion; at Huettelsdorf where a barrel with iron hoops, containing 5.6 kilos of dynamite in cartridges, thrown from a height of 33 meters on to the rocks, was recovered intact; and at Stockholm, where a weight of 100 kilos was allowed to fall from a height of 7 meters upon a box filled with dynamite, the blow being sufficient to smash the box, without producing an explosion. Its sensitiveness to blows, however, increases very rapidly with the temperature, so that, according to Eissler,* "at 350° F, the fall upon it of a dime will explode it." At ordinary temperatures dynamite may be exploded by musket balls which penetrate the mass. Ex-

*Modern High Explosives 62; 1884.

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periments made in Austria (1871) showed that the certainty of explosion depends somewhat upon the nature of the envelope; at 60 paces the Werndl musket exploded dynamite in a wooden case at every shot, and at a greater distance when in a metal case; but that the explosives may be exposed without danger to infantry fire at from 1500 to 2500 paces, depending on the nature of the case. These numbers must undoubtedly be increased for more modern arms.

The firing point of dynamite is about 180° C (356° F), and at this temperature it either burns or explodes. If free from all pressure, jar, vibration, or force of any kind, it burns; otherwise it explodes. If a thin layer be placed on a plate of tin and heated over a burner it volatilizes or takes fire. If the layer is of any considerable depth, say over a quarter of an inch, it explodes. This is a dangerous experiment. When heated to any temperature less than this, it is exploded by a detonator, blow, jar, or vibration with an ease dependent on the temperature and time of exposure. When ignited in comparatively small quantities it simply burns away fiercely, but with moderate and larger amounts ignition causes explosion. High temperatures much below the firing point may effect dynamite unfavorably by causing the nitroglycerine to exude, or in technical terms, "they will make the powder leak," hence a dynamite should be tested and made to resist exudation at the highest temperature to which it may be exposed.

Dynamite freezes at about 40° F, and remains frozen at temperatures considerably exceeding this. If solidly frozen it cannot be detonated, except with great difficulty and uncertainty, but if loose and pulverulent it may be detonated, though the violence is much diminished, hence when frozen it is practically useless as a blasting agent

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and must be thawed or "tempered." This operation requires great care, and the instructions issued with each package should be closely followed. Many foolish persons suppose that, since it is reasonably safe to ignite a cartridge of unfrozen dynamite, it is equally safe to warm it upon a shovel, or in an oven, or in a tin vessel over a fire, or in various other ways which usually lead to a verdict of "accidental death," but would be more properly designated as suicide or manslaughter. It cannot be too strongly impressed upon the minds of those handling it that if dynamite or other nitro-glycerine preparations are gradually warmed up to a temperature approaching their exploding points they become extremely sensitive to the least shock or blow, and once that point is reached they do not simply ignite, but they explode with great violence, and further that, owing to the poor conductivity of the mass, a portion of it which is in contact with the source of heat may become raised to this temperature, while the rest of the mass is much below it.

Frozen dynamite is much less sensitive to a blow or to the impact of a projectile than unfrozen, but it is much more susceptible to explosion by ignition. For instance, so small a quantity as one pound has been exploded when frozen, while larger quantities of the unfrozen material have burnt away without explosion.

The commercial success attending the invention of dynamite No. 1 led others to examine the fitness of other materials for this use, and a great variety of mixtures under a variety of names were put upon the market, the best among them being Mowbray's Mica Powder, in which minute scales of finely comminuted mica were used as the absorbent. He claimed for this powder a greater brusqueness of action than obtains with kiesel-

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guhr dynamite on the ground that in this powder the nitro-glycerine was wholly held superficially on the plates, while with the kieselguhr it was partially held in interstices within the skeletons, and that as a consequence the explosive reaction would travel more rapidly in the first than in the second. This is a nice point, but the results obtained by General Abbot* tend to demonstrate its reality.

Early in the employment of dynamite it became apparent that dynamite No. 1 possessed certain disadvantages, among which were its great power and the violence of its action, which rendered it inapplicable for certain kinds of work, such as mining coal and quarrying rock for building stones, since it reduced the coal to powder and broke the rocks into fragments, while it was less efficient than black powder for many other kinds of work, as in soft rock and earth. It may be summed up that, in general, the harder and firmer the material to be blasted the more effective proportionally will the violent explosive be, while in soft material the reverse holds true. In hard rock the violent, momentary shock has an irresistible shattering effect, which is rapidly propagated through the dense material and thus becomes widely extended, while the material is strong enough to resist to a high degree the slowly developed pressure of the black powder. In soft material the great force of the violent explosive, suddenly applied, may act to move or compress the particles in the immediate neighborhood of the explosion, while the slower, accelerating force of the black powder will be transmitted over a large area and will cause the displacement of large masses. Hence the circumstances may be such that the less powerful explosive becomes the more efficient agent.

*Exps. on Submarine Mines 93; 1881.

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As the energy of dynamite No. 1 and its method of manifestation is dependent on the nitro-glycerine it contains, it seems apparent that, in order to reduce this energy and moderate the violence of the explosion, we have only to reduce the percentage of nitro-glycerine contained in it, and practice shows this to be efficacious, but only up to a certain point, namely, where the proportions are reduced to 30 percent of nitro-glycerine, for it is asserted by Howe* that a kieselguhr dynamite containing less than 30 percent of nitro-glycerine cannot be exploded. If, however, we use a powder such as gunpowder, or one which contains combustible and oxidizing materials similar to those which exist in gunpowder, we shall obtain an absorbent (technically known as an absorbent base or dope) which will retain considerable quantities of nitro-glycerine and yet be capable of being detonated even when it contains less than five percent. An almost infinite number of such mixtures may be made and many have been used.

Owing to the explosive nature of the materials used as the absorbent in these latter mixtures certain writers have divided the dynamites into two groups:

1. Dynamites with an inert base.
2. Dynamites with an active base.

Examples of the first are given in the following table, and, although the bases are styled inert, it will be observed that some of the bodies used are combustible, and it is possible that they may be more or less consumed by a portion of the oxygen of the nitro-glycerine. Carbo-dynamite is such a powder. This is a recently invented one, and has attracted attention from the highly-attracting and retentive power of the base. This charcoal will absorb and retain nine times its weight

*Proc. Nav. Inst. 10, 226; 1884.

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of nitro-glycerine. Of course the different dynamites contain varying proportions of neutralizing carbonates.

DYNAMITES WITH INERT BASES.

Name of Dynamite.	Absorbents.
Nobel's Dynamite No. 1,	kieselguhr.
Giant powder No. 1,	"
Dynamite blanche de Paulilles,	"
Dynamite de Vonges,	"
E. C. dynamite,	"
S. 1. dynamite,	"
Rutenberg's explosive	"
Dynamite rouge,	"
Hill's powder,	precipitated silica.
Mowbray's mica powder,	mica scales.
Asbestos powder,	asbestus.
Hercules powder (Extra No. 1),	magnesia alba.
Magnesia powder,	" "
Nitro-magnite,	" "
Dyna-magnite,	" "
Dynamite de Boghead,	ashes of Boghead mineral.
Selenitic powder,	plaster of Paris.
Horsley's powder No. 1,	alum and magnesium sulphate.
Metalline nitroleum,	red lead and plaster of Paris.
Rhenish dynamite Co.,	kieselguhr and naphthalene.
Dynamite noire,	sand and coke.
Mataziette,	sand, ochre, charcoal and resinous matter.
Porifera nitroleum,	sponge or vegetable fibre and plaster of Paris.
Burstenbender's explosive,	spongy vegetable substances with glycocoll or chondrin.
Morse's explosive,	rosin.
Fulgurite,	coarsely-ground farinaceous substance, preferably corn meal.
Carbo-dynamite (Borland's),	charcoal from cork.

The dynamites with active bases may be conveniently classified in several groups, depending on the chief characteristic of the base. Of course there will be great variations in the compositions of the different dynamites classed in the same group, as, for instance, those with a gunpowder base, where one base may contain potassium nitrate, another sodium, another ammonium, and another all three of these nitrates or some other oxidizing agent;

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where the combustible substances may be charcoal, starch, sugar, coal, peat, naturally decayed wood, sulphur, and a multitude of others, except sawdust; where the proportions may vary to an infinite extent; and where the state of aggregation and outward form may vary to an equal extent. It is owing to the great extent to which these possible variations have been availed of that I have concluded that it is unnecessary to go into a minute description of these dynamites, even if the time allotted would permit me, and simply to group them so that their general characters could be seen at a glance.

DYNAMITES WITH GUNPOWDER BASES.

Ammonia dynamite,
Ammoniakkrut,
Ammonic powder,
Coad's explosive,
Champion's powder,
Colonia powder,
Dittmann's powder,
Dynamite No. 2,
Dynamite au charbon,
Dynamite d'ammoniaque,
Dynamite grises de Paulilles,
Extra powder,
Fowler's explosive,
Giant powder No. 2,
Gotham's powder,
Hercules powder,
Horsley's powder No. 2,
Judson powder,
Jupiter powder,
Lithofracteur,
Monakay's explosive,
Miner's Powder Co. dynamite,
Neptune powder,
Potentia,
Petrolithe,
Sebastine,
Thunderbolt powder,
Titan powder,
Virite powder,
Vulcan powder.

Although the dynamites which contain sawdust, together with oxidizing agents are really dynamites with gunpowder bases, I have separated them from the previous group because they have attracted especial attention under the name of lignin-dynamites, and because, too, that these dynamites possess the special advantage of resisting the action of water, that is, that water does not cause the nitro-glycerine to exude from them as it does from the No. 1 and other dynamites.

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LIGNIN—DYNAMITES.

Ætna powder,	Miner's Friend powder,
Atlas powder,	Petralithe,
Brain's powder,	Rendrock,
Dualin,	Rhexite,
Dynamite de Krummel,	Safety nitro-powder,
Dynamite de Lanky,	Schultze's dynamite,
Hecla powder,	Vigorite.

In the next group I have placed those dynamites in which the base is partly or wholly composed of cellulose nitrate; either the soluble or insoluble variety, or that made from cotton, wood pulp or any variety of cellulose; and mixed with a variety of other substances, omitting, however, those made with explosive gelatine or similar substances.

For the sake of brevity I will style these

DYNAMITES WITH GUN—COTTON BASES.

Cellulose dynamite,	Paleine,
Clark's explosive,	Punshon's explosive,
Dean's explosive,	Schultze's dynamite,
Dittmann's explosive,	Straw dynamite,
Glyoxiline,	Trauzl's dynamite.

The theory upon which these are formed is seen from the following equations:

$$4(C_3H_5)O_3(NO_2)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2,$$

$$2(C_6H_7O_2)O_2(NO_2)_3 = 9CO + 3CO_2 + 7H_2O + 3N_2,$$

where it is shown that when nitro-glycerine is detonated free oxygen is evolved, while when gun-cotton is detonated carbon monoxide, which is a product of incomplete combustion, is produced. Now, if we mix the two explosives in the proper proportions we ought to obtain complete combustion without any uncombined oxygen being liberated, and, under these circumstances, we ought to obtain a more powerful explosive than we have in either of the constituents alone. As a fact, these proportions

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are only realized in explosive gelatine, and the explosives given above are simply dynamites with powerfully explosive bases.

Besides these we have dynamites formed by mixing nitro-glycerine with other explosive nitrates than the cellulose nitrates, such as *Glukodine*, consisting of nitro-glycerine and nitro-saccharose, and *Thunder Powder*, consisting of nitro-glycerine and nitro-glucose.

Glukodine is made by mixing glycerine and cane sugar together and treating the mixture as for making nitro-glycerine.

Thunder powder is made by mixing glycerine and honey and treating them in the same way as above. The products in each case are mixed with an explosive dope, generally a lignin one.

Explosive or combustible nitro-substitution compounds are also used for, or as constituents of, the dynamite dopes, as in *Castellano's powder*, where the dope consists of fibrous material and pulverized earth containing nitro-benzene; or in *Engel's powder*, which contains pyroxyline, pyropaper, nitro-starch, nitro-mannite, nitro-benzene, water-glass and mineral nitrates.

I have by no means exhausted the list of dynamites, but I have aimed to give examples from among the better known of each group.

In estimating the potential energy of a dynamite with an inert base, such as kieselguhr dynamite, we cannot neglect the effect of the base, for though it is inert as far as any chemical effect is concerned, it is not so as regards the physical effect. Thus, as we have seen, the energy of an explosive depends upon the quantity of gas liberated and the temperature to which this gas is raised; the the pressure exerted, for a density of loading of unity, depends upon the volume of the products of the explo-

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sion, when unconfined, as compared with the volume of the explosive from which they are produced; and the efficiency of the explosive depends upon the nature of confining envelope, the physical condition of the explosive, the manner in which the explosive reaction is generated and propagated, and the speed with which the propagation takes place. Now, with Nobel's dynamite No. 1 the quantity of gas liberated and the heat evolved will be the same as would result from the nitro-glycerine contained in it if that mass of nitro-glycerine were by itself, but the temperature of the gas, and hence its volume, and therefore the resulting pressure for unit volume will be less, owing to the fact that a considerable portion of the heat evolved is expended in heating the kieselguhr. Taking the specific heat of the kieselguhr to be the same as that of the compressed gases (and this is sufficiently exact) one-fourth of the total heat evolved will be expended in this way. With this assumption, together with the data given on pages 25 and 26 of Lecture IX, we can calculate approximately the pressure which such a dynamite would give for a density of loading of unity.

Thus, in a mass of 75 percent dynamite, weighing 227 grams (that is, a mass equal to the molugrams of nitro-glycerine), there will be

$$.75 \times 227 = 170.25 \text{ grams of nitro-glycerine,}$$

which will yield

$$.75 \times 161.82 = 121.37 \text{ liters of gas at } 0° \text{ and } 76 \text{ cm.,}$$

and these 170.25 grams in burning will yield

$$.75 \times 356500 = 267375 \text{ calories.}$$

Having assumed that the specific heat of the kieselguhr is the same as that of the compressed gases, the numer-

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ical value of $W_1S_1 + W_2S_2 +$ etc. will remain unchanged and, therefore, the calorific intensity will be

$$\frac{267375}{62.24} = 4296° \text{ C},$$

$$\text{whence } V' = \frac{121.37 \times 4569}{273} = 2031 \text{ liters},$$

or one gram of dynamite will yield

$$\frac{2031}{227} = 8.95 \text{ liters},$$

and, the density of the dynamite being 1.6, one cubic centimeter will yield 14.32 liters of gas.

To find the pressure for a density of loading of unity we must take into consideration the fact that the solid remains unchanged and, as the density of the dynamite is the same as that of nitro-glycerine, the volume of the vessel will be reduced by that of the kieselguhr, hence it will be

$$\frac{14320}{.75} = 19093 \text{ atmospheres or } 125.3 \text{ tons}.$$

The efficiency of a dynamite with a gunpowder base has been in the past a matter of dispute. Of course the constituents of the base may be such, and be mixed in such proportions, as to be of little or no value, but, on the other hand, the constituents and proportions may be those of the best gunpowder. Granting the last conditions, there have been some who have held that the gunpowder could add nothing to the effect, as the explosive reaction is propagated so rapidly in the nitro-glycerine that the work is done before the gunpowder begins to act. As a fact, experience in practice, and experiments made with testing machines,* show that such dynamites do more work than the nitro-glycerine

*Drinker's Explosive Compounds 73–86; 1883.

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present in them would do when alone. This may be explained as follows:

When gunpowder is exploded by ignition the explosive reaction is propagated in a comparatively slow and progressive manner, and hence the heat evolved is dissipated to such an extent that the temperature of the gases falls below the theory. When gunpowder is detonated the propagation of the explosive reaction is more nearly instantaneous, a higher temperature is produced, a greater volume of gas is developed, and the mass is able to do more work. If gunpowder be mixed with nitro-glycerine and the latter be detonated the gunpowder will probably be detonated also, and the resulting force will be the sum of the forces of the two explosives, and they will operate at nearly the same time.

When discussing the composition of gunpowder it was pointed out that many cheaper oxidizing agents had been proposed for use in place of the potassium nitrate, but that the principal ones were unfit for this use as they are deliquescent. Such salts are, however, used in the gunpowder dopes, and it is claimed that their presence makes the dynamite unfit to bear climate changes and makes it especially dangerous in warm or drying weather.*

As it may sometimes be desirable to ascertain if a substance contains nitro-glycerine, the following tests may be applied: If a liquid is oozing out, or can be squeezed out from the substance, put the drop on blotting-paper. If this is nitro-glycerine it will make a greasy stain, not disappearing or drying away; struck with a hammer on iron, it will give a loud report; lighted and burnt, it will give a crackling sound and a yellowish to greenish flame; gradually heated by a flame beneath, it will give a sharp report.

*Proc. Nav. Inst. 664–665; 1885.

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Again, put a portion in a test tube and shake it up with alcohol, (methyl alcohol is best), having first ascertained that the alcohol alone produces no turbidity when poured into water. After shaking, filter the contents of the test tube into another tube and add pure water to the latter. If nitro-glycerine is present the liquid will become milky and, on standing, the nitro-glycerine will eventually collect at the bottom as a heavy lustrous liquid.

A much more delicate test is with aniline and concentrated sulphuric acid. In the presence of nitro-glycerine a purple color is produced which changes to green on the addition of water.

We have shown that when gun-cotton is exploded the products are those of incomplete combustion, and hence it is not surprising to learn that it has been long since proposed to mix oxidizing agents with the gun-cotton in order to obtain more complete combustion. Such mixtures have been prepared for use as projecting agents in small arms and for blasting. As it has been found desirable to produce the explosive either in a granular or some other regular form, cementing agents, such as gum, resins, paraffine, and the like, have been used for causing the particles to cohere. In the following list the names of some of the explosives made in this way are given:

GUN–COTTON POWDERS.

Name.	Admixtures.
Abel's,	Potassium or sodium nitrate, or potassium chlorate or mixtures thereof.
Bantock's,	Potassium nitrate and chlorate with a neutral salt.
Cotton powder,	Barium nitrate and paraffine.
Di-Flamyr,	Potassium nitrate.
E. C. powders,	Cellulose, potassium and barium nitrates, coloring matter.
Huetter's blasting compound,	Barium nitrate and paraffine.
Liverpool cotton powder,	" " " "

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Mackie's,	Potassium nitrate and resin, or similar substances.
Nitrated gun-cotton,	Any nitrates
Plera,	With or without nitrates, and with resin or similar substances.
Potentite,	Potassium nitrate and paraffine.
Punshon's gun-cotton,	Potassium nitrate and sugar.
Rifle gun-cotton,	Like Plera.
Robertson's,	Potassium chlorate and collodion.
Tonite,	Like Cotton powder.
Tonkin's,	Potassium or sodium nitrates, charcoal and sulphur.

Besides these we have a powder proposed by *Johnson* in which soluble gun-cotton is to be used. This is dissolved in a solution of camphor, intimately mixed with potassium or barium nitrates, and charcoal or other carbonaceous material, and the solvent evaporated. Evidently we thus obtain a nitrated celluloid.

For convenience sake I have separated into a second group the explosive mixtures made from cellulose nitrates obtained from wood and similar materials. Cellulose nitrate from wood is called Nitro-lignin, and hence we we will style this group

NITRO—LIGNIN POWDERS.

Name	Admixtures.
Clark's,	Potassium or sodium nitrates, alum or tannin, collodion.
Cooppal's,	With or without a nitrate or nitrates, and starch.
Lannoy's,	Sodium nitrate and sulphur.
Lanfrey's,*	Potassium nitrate, charcoal, dextrin.
Schultze's gunpowder,	Potassium and barium nitrates, paraffine and coloring matters.
Smokeless powder,	Ditto.

Patent gunpowder, sawdust gunpowder and wood gunpowder are practically the same as smokeless gunpowder. The advantages claimed for these powders for use in guns is that they generate but little smoke, impart but a slight recoil, produce but a mild report, and leave little

*Nitro-lignin from straw.

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or no residuum to foul the piece. These are most desirable qualities, and the possession of such a powder, if it were safe and certain also, would give an army a decided tactical advantage over an enemy who used the ordinary gunpowder. Many of these powders have, owing to these qualities, been used to some extent for sporting purposes, but, unfortunately, they have sometimes developed such abnormal pressures as to burst the gun, and this is a condition which is more likely to obtain in great guns than in fowling-pieces or muskets; and in muskets which are fired so rapidly during an engagement as to become quite warm, than in fowling-pieces, which are discharged so infrequently that the barrel remains cool.

As has been said, the theoretically complete combustion of gun-cotton and of nitro-glycerine is only realized in the explosive invented by Nobel, which is known as Explosive Gelatine, but which is also termed Gum Dynamite and Blasting Gelatine This substance is produced by dissolving soluble gun-cotton in nitro-glycerine by the aid of heat, and, when the solution is complete, allowing the mass to cool. The product solidifies to a gelatinous paste which has a honey yellow color and a consistency varying from that of a tough leathery material to that of ordinary jelly, these differences being dependent upon the chemical condition of the cellulose nitrate used, the amount present, and the method of manipulation followed during manufacture. The percent of cellulose nitrate varies from four to eight. The mixing is performed in a metal vessel set in a water bath in which the nitro-glycerine is heated to about 100° F. The well-washed and purified, and dried cellulose nitrate is then added in portions and stirred in as fast as it dissolves.

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As thus prepared, explosive gelatine has a density of 1.6. It does not absorb water and, when placed in it, it is unaffected, except superficially, a small quantity of nitro-glycerine being dissolved from the surface which thus becomes blanched, but no further action takes place, no matter how long the explosive remains immersed, as the cellulose nitrate which is thus separated acts as an impermeable coating to protect the surface.

Explosive gelatine burns in the open without explosion when we operate on small quantities and avoid previous heating, but, if heated to its ignition point when confined, it explodes. It has been maintained for eight days at a temperature of 70° C (158° F) without showing any signs of decomposition. Heated slowly it explodes at 204° C (399.°2 F), heated rapidly, at 240° C (464° F).

At low temperatures it freezes into a hard whitish solid with a crystalline structure, but the exact temperature at which freezing takes place has not been definitely ascertained,* as some cartridges are found to resist freezing for twenty-four hours, although, during that time, they are kept in a mixture of ice and salt, while others freeze readily at 2° to 4° C (35° to 40° F).

Explosive gelatine is much more insensitive than any of the other high explosives, special strong detonators, or ordinary detonators with gun-cotton or dynamite primers being required to explode it, and it requires confinement to develop its full power, or rather its capacity for transmitting the explosive reaction, for a train of it cannot be exploded except by means of a very powerful initial detonation. Hence it is quite insensitive to explosion by influence or to the impact of balls. This insensitiveness, however, varies in the different grades, and, in general terms, it may be said that the thinner

*Proc. Nav. Inst. 11, 95; 1885.

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the gelatine the more sensitive it becomes. Its sensitiveness increases when it becomes frozen, and it may then be readily detonated, while it can also be exploded by the impact of balls.

The sensitiveness of this explosive is still more diminished by adding to it camphor or other substances rich in carbon and hydrogen, such as benzene or nitro-benzene. These bodies are soluble in the nitro-glycerine and may be readily introduced in the process of manufacture. Military Explosive Gelatine is such a mixture, and consists of explosive gelatine to which about four percent of camphor has been added. Its appearance is similar to ordinary explosive gelatine, but it emits the odor of camphor, and, with the exception of the increased insensitiveness, its properties are the same. By this addition of camphor the temperature at which it explodes has been raised to from 300° to 330° C (572° to 626° F).

Berthelot* finds the theoretical pressure of explosive gelatine to be nearly identical with that of nitro-glycerine. F. von Rziha† finds its theoretical efficiency to be less than that of nitro-glycerine, the ratio being as 1.4 : 1.45, and, from the discussion of extensive data obtained in blasting, he finds that the same relation holds true in practice. Gen. Abbot,‡ however, finds the relative intensities in the horizontal plane for No. 1 dynamite, nitro-glycerine and explosive gelatine when fired under water, to be 100 : 81 : 117, while in a later determination§ of a sample of explosive gelatine furnished by Nobel's Explosives Co. of Glasgow, he obtained a relative intensity of 142. The higher results obtained by Gen. Abbot may be due to the comparative slowness with which the detonation is propagated in this explosive, by which it

*Sur la force des matieres explosive 2, 224; 1883.
†Proc. Nav. Inst. 13, 234–240; 1887.
‡Loc. cit 9, 757; 1883.
§Loc. cit 11, 282; 1885.

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has a longer interval for doing work on the metal of the pressure gauge than the nitro-glycerine has, and that this greater persistence of action enables it to produce a more marked impression.

Berthelot* holds that the effect of the camphor, in increasing the insensitiveness of the explosive, results from the increased elasticity and solidity which the explosive thus acquires, in consequence of which the initial shock of the detonator is propagated through a much greater mass of the substance than it would be if the camphor were not present, so that the sudden and local elevation of the temperature, which is necessary for inducing the chemical and mechanical action which results in detonation, is not realized except by the use of a very powerful initial detonator. Camphor, according to this theory, does not exert any action on discontinuous powders, and this is shown in practice with potassium chlorate powder.

Owing to its solid form and plastic nature, its great power and its insensitiveness, explosive gelatine has been regarded as the ideal military explosive, but, unfortunately, it has in several instances become decomposed during storage and without any apparent cause. One such case occurred in my own experience,† and others are recorded elsewhere, and, while this decomposition proceeded quietly and did not produce an explosion, yet it constitutes an element of danger in the use of this explosive.

The heat test‡ for explosive gelatine and gelatine dynamite is applied by intimately incorporating 50 grains of the explosive with 100 grains of French chalk and then proceeding as with gun-cotton, and the sample to pass

*Proc. Nav. Inst. 9, 747; 1883.
†Jour. Am. Chem. Soc. 6, 7–8; 1884.
‡Rept. H. M. Insp. Exp. 63; 1884.

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should withstand a temperature of 71.°1 C (160° F) for ten minutes.

The test for liquefaction is made by cutting a cylinder from the mass to be tested, whose length is about equal to its diameter, the bases of the cylinder being flat. The cylinder is then to be placed on end on a flat surface, without any wrapper, and secured by a pin passing vertically through its center. In this condition the cylinder is to be exposed for 144 consecutive hours (six days) to a temperature ranging from 85°–90° F (inclusive), and during such exposure the cylinder shall not diminish in length by more than one-fourth, and the upper base shall retain its flatness and sharpness of its edge.

The test for liability to exudation requires that there shall be no separation from the general mass of the sample to be tested, of a substance of less consistency than the bulk of the remaining portions of the material, under any conditions of storage, transport or use, or when the material is subjected three times in succession to alternate freezing and thawing, or when subjected to the liquefaction test above described.

For use in blasting, explosive gelatine is mixed with various explosive dopes, just as nitro-glycerine and gun-cotton are, so as to cheapen the cost, reduce the violence of the explosion, and produce a more slowly acting explosive. These bodies may be termed Gelatine Dynamites, and the principal ones put upon the market are given in the following table:

GELATINE DYNAMITES.

Name.	
Ammonia gelatine,	Ammonium nitrate and charcoal.
Blasting gelatine No. 1,	A nitrate with or without charcoal.
Forcite,	Potassium nitrate, lignin and dextrine.
Gelatine dynamite,	Potassium nitrate and lignin.
Gelegnite,	" " " "
Warren's powder,	Gun-cotton and gunpowder.

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Reference books, *Hill's Notes, Cundill's Dict. of Explosives, Eissler's Modern High Explosives, Berthelot, Desortiaux, Chalon's des Explosifs Modernes, Drinker's Tunnelling and Explosive Compounds*, 1883; *Proc. Nav. Inst.*

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LECTURE XI.

The Phenomena accompanying Explosions and the Theories which have been proposed to Explain Them.

The effect produced by an explosive is caused by the blow or impulse imparted through the rapid production from it of a large volume of highly heated gas. The explosive character of the change depends —

1st. Upon the great change of state produced.

2d. Upon the time required for the change to take place.

Both these causes operate to a greater or less extent in all explosive reactions. When both are fully exerted the most energetic chemical reaction, or, in other words, the most violent explosion takes place. The differences exhibited in explosions and by explosive bodies depend upon the different manner and proportions in which these causes act. Thus, nitro-glycerine is much more powerful and violent than gunpowder, because it generates a larger volume of gas in a shorter time, while fulminating mercury is not more powerful than gunpowder, because the quantity of gas given off, and the temperature of the reaction are less, but it is more violent, because the decomposition goes on more quickly.

The kinds and quantity of gas given off in an explosive reaction depend upon the chemical composition of

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the explosive body and the character of the decomposition. The heat evolved during the reaction adds to the effect by increasing the tension (expanding the volume) of the gas formed. The heat given off in a reaction is an absolute quantity, the same whether the reaction goes on slowly or rapidly. But the *explosive* effect will evidently greatly depend upon the *rapidity* of the formation and expansion of the gas. Thus, if an explosive undergoes the same change under all circumstances of firing, the force developed will always be the same, but the *explosive effect* will be increased as the time of action is lessened.

Explosions are greatly affected by the circumstances attending them. Different substances, of course, give different results, owing to their different compositions and reactions, but we also find that the same substance will exercise a different explosive effect when fired under certain conditions from what it does when fired under other conditions, as these may affect either the rapidity or the products of the chemical change.

The circumstances attending an explosion may be generally considered under—

1st. Physical or mechanical condition of the explosive body itself.

2d. External conditions.

3d. Mode of firing.

Many instances may be cited which illustrate the influence which its state exerts upon the explosive reaction which takes place in a given substance. Thus, nitro-glycerine at a temperature above 40° F is a liquid, and in the liquid condition may be violently exploded by a fuse containing 15 grains of fulminating mercury. Below 40° it freezes and cannot be so fired except with great difficulty.

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The advantage of dynamite over nitro-glycerine lies principally in the fact that the latter is presented in another mechanical condition, more convenient and safer to use than the liquid form, the nitro-glycerine being the same chemically in either case, but it would seem also that the subdivision of the nitro-glycerine thus effected modifies the rate of propagation of the explosive reaction.

The same mixture of charcoal, sulphur, and saltpetre gives a very different effect if made up into large grains from what it does if made up into small ones.

Gun-cotton presents the most marked example of the effect of mechanical state, since it can be prepared in so many ways. If flame is applied to loose uncompressed gun-cotton it will flash off; if it is spun into threads or woven into webs, its rate of combustion may be so much reduced that it can be used in gunnery or for a quick fuze; powerfully compressed and damp, it burns slowly; dry gun-cotton may be exploded by a fulminate fuze; wet gun-cotton requires the initial explosion of a small amount of dry.

Confinement is necessary in order to obtain the full effect of all explosives, since the most rapid explosion requires a certain time for its accomplishment, but as the time required is less, the amount of confinement necessary is less, hence, with the sudden or violent explosives, the confinement required may be so small that its consideration may be practically neglected. For instance, large stones or blocks of iron may be broken by the explosion of nitro-glycerine laid upon their surfaces in the open air. Here the atmosphere itself acts as a confining agent, the explosion of the nitro-glycerine being so sudden that a very considerable mass of air is set in motion, and hence offers its resistance.

Another example is found in nitrogen chloride, which

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is one of the most sudden and violent of all explosives. In its preparation it is precipitated from a watery liquid, and it is therefore, when used, wet or covered with a very thin film of water. This thin film of water, which is not more than $\frac{1}{1000}$ of an inch in thickness, supplies a necessary and sufficient confinement for the explosive, and if it is removed the explosive effect is much diminished.

Gunpowder, on the other hand, requires strong confinement, since its explosion is comparatively slow. Thus, unless the case used in firing a charge of gunpowder under water is strong enough to resist the pressure of the gases until the action has become general, it will be broken, and a large amount of the powder thrown out unburned. This result is often produced when firing large-grained powder in heavy guns. The ball leaves the gun before all the powder has burned, and grains or lumps of it are thrown out uninjured. However, the confinement needed by the slower explosives may be diminished by igniting the charge at many points, so that less time is required for its complete explosion. Hence in the gunpowder spar torpedo issued from this Station, while only one fuze was used, this was placed in the hollow spindle which traversed the center of the torpedo, and which was pierced with many holes, through which the flame from the fuze passed from the main charge.

The way in which the atmosphere plays the part of a tamping agent, when high explosives are detonated in the open, is very lucidly explained by Prof. J. P. Cooke.* After describing experiments made at this Station some years ago, in which rocks were shattered by charges of dynamite, which were detonated unconfined on their surfaces, he says:

*The New Chemistry 229–233; 1882.

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On inspecting the equation representing the change taking place during the explosion of nitro-glycerine we see "that the chemical action is very nearly the same as in the burning of gun-powder, the difference being that, while in the powder the carbon and oxygen atoms belong to different molecules, in nitro-glycerine they belong to the same molecule. In both cases the carbon burns, but in the nitro-glycerine the combustion is within the molecule. This difference, however, which the theory indicates, is one of great importance, and shows itself in the effects of the explosion.

"In gunpowder the grains of charcoal and nitre, although very small, have a sensible magnitude, and consist each of many thousand, if not of many million molecules. The chemical union of the oxygen of the nitre with the carbon atoms of the charcoal can take place only on the surface of the charcoal grains; the first layer of molecules must be consumed before the second can be reached, and so on. Hence the process, although very rapid, must take a sensible time. In the nitro-glycerine, on the other hand, the two sets of atoms, so far from being in different grains, are in one and the same molecule, and the internal combustion is essentially instantaneous. Now, this element of time will explain a great part of the difference in the effect of the two explosions, but a part is also due to the fact that nitro-glycerine yields fully nine hundred times its volume of gas, while with gunpowder the volume is only about three hundred times that of the solid grains. There is a further difference in favor of the nitro-glycerine in the amount of energy liberated, but this we will leave out of account, although it is worthy of notice that energy may be developed by internal molecular combustion as well as in the ordinary process of burning.

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"The conditions, then, are these: With gunpowder we have a volume of gas, which would normally occupy a space three hundred times as great as the grains used, liberated rapidly, but still in a perceptible interval. With nitro-glycerine a volume of gas, nine hundred times that of the liquid used, is set free, all but instantaneously. Now, in order to appreciate the difference of effect which would follow this difference of condition, you must remember that all our experiments are made in air, and that this air presses with an enormous weight on every surface. If a volume of gas is suddenly liberated, it must lift this whole weight, which, therefore, acts as so much tamping material. This weight, moreover, cannot be lifted without the expenditure of a large amount of work. Let us make a rough estimate of the amount in the case of nitro-glycerine. We will assume that in the experiment at Newport the quantity exploded yielded a cubic yard of gas. Had the air given away instead of the rock, the liberation of this volume of gas must have lifted the pressure on one square yard (about nine tons) one yard high, an amount of work which, using these large units, we will call nine yard-tons or about 60,000 foot-pounds. Moreover, this work must have been done during the excessively brief duration of the explosion, and, it being less work to split the rock, it was the rock that yielded and not the atmosphere. Compare now the case of gunpowder. The same weight of powder would yield only one-third of the volume of gas, and would, therefore, raise the same weight to only one-third of the height; doing, therefore, but one-third the amount of work, say 20,000 foot-pounds. Moreover, the duration of the explosion being at least one hundred times longer than before, the work to be done in lifting the atmosphere during the same exceedingly short interval

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would be only $\frac{1}{100}$ of 20,000 foot-pounds, or 200 foot-pounds, and, under these circumstances, you can conceive that it might be easier to lift the air than to break the rock.

"If there are some who have not followed me through this simple calculation, they may, perhaps, be able to reach clear views upon the subject by looking at the phenomena in a somewhat different way. It can readily be seen that the sudden development of this large volume of gas, which becomes at once a part of the atmosphere, would be equivalent to a blow by the atmosphere against the rock; or, what would be a more accurate representation of the phenomenon, since the air is the larger mass, and acts as an anvil, a blow by the rock against the air. It may seem very singular that our atmosphere can act as an anvil, against which a rock can be split, and yet it is so, and, if the blow has velocity enough, the atmosphere presents as effective a resistance as would a granite ledge. The following consideration will, I think, convince you that this is the case: I have here a light wooden surface, say one yard square; the pressure of the air against the surface is equal, as I just stated, to about nine tons; but the air presses equally on both sides, and the molecules have such great mobility that, when we move the surface slowly, they readily give way, and we encounter but little resistance. If, however, we push it rapidly forward, the resistance greatly increases, for the air molecules must have time to change their positions. and we encounter them in their passage. If now we increase the velocity of the motion to the highest speed ever attained by a locomotive — say, one and one-fifth mile per minute — we should encounter still more particles, and find a resistance which no human muscle could overcome. Increase that velocity ten times,

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to twelve miles a minute, the velocity of sound, and the air would oppose such a resistance that our wooden board would be shivered into splinters. Multiply again the velocity ten times, and not even a plate of boiler iron could withstand the resistance. Multiply the velocity once more by ten, and we should reach the velocity of the earth in its orbit, about 1200 miles a minute, and, to a body moving with this velocity, the comparatively dense air at the surface of the earth would present an almost impenetrable barrier, against which the firmest rocks might be broken to fragments. Indeed, this effect has been several times seen, when meteoric masses, moving with these planetary velocities, penetrate our atmosphere. The explosions which have been witnessed are simply the effect of the concussion against the aeriform anvil at a point where the atmosphere is far less dense than it is here. So, in the case of the nitro-glycerine, the rock strikes at the atmosphere with such a velocity that it has the effect of a solid mass, and the rock is shivered by the blow."

In any explosive reaction the mode of bringing about the change exercises an important influence. The application of heat, directly or indirectly, is the principal means of causing an explosion. Thus, as shown in Lecture III, in gunnery, the flame from the percussion cap or primer directly ignites the charge; so also a fine platinum wire heated by an electric current will ignite explosive material, which is in contact with it. Friction, percussion, concussion, produce the same effect indirectly, but their action is modified by the surrounding conditions. Thus, Abel says* regarding the second, that "the readiness and certainty with which gunpowder, gun-cotton, nitro-glycerine and other explosive substances

*Phil. Trans. 159; 1869.

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may be exploded through the agency of a blow from a hammer or falling body are regulated by several circumstances; they are in direct proportion to the weight of the falling body, to the height of its fall, or the force with which it is impelled downwards, to the velocity of its motion, to the mass and rigidity or hardness of the support or anvil upon which the body falls, to the quantity and mechanical condition of the explosive agent struck, and to the ready explosibility of the latter. Thus a sharp blow from a small hammer upon an iron surface will detonate gunpowder with a much greater certainty than the simple fall of a heavy hammer or a comparatively weak blow from the latter. It is very difficult by repeated blows, applied at very brief intervals, to ignite gun-cotton, if placed upon a support of wood or lead, both of which materials yield to the blow, the force set in operation by that blow being transferred through the explosive agent and absorbed in work done upon the material composing the support. If, however, the latter be of iron, which does not yield permanently to the blow of the hammer, the detonation of these substances is readily accomplished. If the quantity of the explosive agent employed be so considerable as to form a thick layer between the hammer and support, the force applied appears to be to so great an extent absorbed in the motion imparted to the particles of the compressible mass, that its explosion is not readily accomplished; and if the material be in a loose or porous condition (as *e. g.* in a state of powder or loose wool) much work has to be accomplished in moving particles of the mass through a comparatively considerable space, and a second or third blow is therefore required to determine explosion.

"These circumstances appear to support the view that the explosion of an explosive through the agency of a

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blow is the result of the development of heat sufficient to establish energetic chemical change, by the expenditure of force in the compression of the material or by the friction of the particles against each other. It is conceivable that, from either of these causes, sufficient heat may be accumulated, with almost instantaneous rapidity, in some portions of the mass struck, to develop sudden chemical change." An explosion such as this, in which the chemical change goes on almost instantaneously throughout the mass, is called a detonation.

It is a peculiarity of a detonating explosion that when produced in a body it may induce a similar explosion in another portion of the same body, either when in contact with it, or even when only near it but not in contact. In fact it may induce such an explosion when separated from the second portion by means of a glass or metal plate, or even a mass of water, so that no heated or ignited particles can be projected from one to the other. Since there is apparently no source of heat present to cause the decomposition of the body, what is the agent which causes the explosion of the second portion? This subject of detonation was experimentally investigated by Abel,* and he obtained some very interesting results. He showed that, not only would a detonating body cause the detonation of another mass of the same body, but that it would cause also the detonation of other bodies. For instance, by detonating mercury fulminate in contact with gun-cotton or nitro-glycerine these bodies were also readily detonated. Only a small quantity of fulminate was required, .32 of a gram (5 grains), when confined in a sheet metal cap and placed in direct contact with the nitro-glycerine or compressed gun-cotton being sufficient to cause the detonation of the latter. He found that a mass of nitro-

*Phil. Trans. 159, 489; 1869.

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glycerine by its explosion would cause the explosion of another mass of nitro-glycerine, even though both were immersed in water. His experiments further showed that a peculiar kind of detonation was required in order to cause the detonation of an explosive. For instance, while the detonation of gun-cotton would cause the detonation of nitro-glycerine in close proximity to it, the detonation of nitro-glycerine would not cause the detonation of gun-cotton. This shows that this property of causing detonation does not depend alone upon the force of the detonants, for we know that nitro-glycerine is more powerful than gun-cotton. Again, silver fulminate, which explodes more violently and sharply than mercury fulminate, is no more efficient in producing the detonation of nitro-glycerine or gun-cotton than mercury fulminate, and nitrogen iodide, and nitrogen chloride, which are the most violent explosives we possess, are very much less efficient in causing detonation than mercury fulminate. In the course of his investigations Abel was led to the conclusion "that a particular explosion or detonation may possess a power of determining at the instance of its occurence similar violent explosions in distinct masses of the same material, or in contiguous explosive bodies of other kinds, which power is independent of or auxiliary to the direct operation of mechanical force developed by that explosion; that as a particular musical vibration will establish synchronous vibrations in particular bodies while it will not affect others, and as a chemical change may be wrought in a body by its interception of only particular waves of light, so some kind of explosions or powerful vibratory impulses may exert a disturbing influence over the chemical equilibrium of certain bodies, resulting in their sudden disintegration, which other explosions, that develop equal or greater mechanical force, are powerless to exercise.

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"He offers the following as being the most satisfactory explanation of the remarkable differences pointed out. The vibrations produced by a particular explosion, if synchronous with those which would result from the explosion of a neighboring substance which is in a state of high chemical tension, will, by their tendency to develop those vibrations, either determine the explosion of that substance, or at any rate greatly aid the disturbing effect of mechanical force suddenly applied, while in the case of another explosion which produces vibrations of a different character, the mechanical force applied by its agency has to operate with little or no aid; greater force, or more powerful detonation must, therefore, be applied in the latter instance, if the explosion of the same substance is to be accomplished." This is known as Abel's theory of Synchronous Vibrations.

That vibrations will induce the decomposition of chemical compounds whose atoms are in a state of unstable equilibrium is a well recognized fact in science, and numerous instances can be cited where advantage is taken of this fact to induce chemical change. The effects of the vibrations which produce heat are too well known to need illustration here. The most marked instances of the action of the vibrations which produce light are the decomposition of the silver salts on the photographic plate, and the decomposition of carbon dioxide in the cells of leaves. The vibrations which produce electricity cause the decomposition of chemical compounds, as is seen in the process of electroplating, etc. Why, then, should not the vibrations which produce sound be also capable of inducing chemical change?

The condition of a compound whose atoms are in a state of unstable equilibrium is probably somewhat similar to that of a Prince Rubert's drop, in which the mole-

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cules are in a state of unstable equilibrium. Separate but the smallest bit from the end of the drop and the whole drop flies to pieces. So with a chemical compound, if by means of vibrations we can increase the amplitude of the vibration of any of its atoms, so that the force of chemical attraction is overcome, the molecule breaks up with violence; and in explosive bodies the violence is increased by the character of the compounds which are formed through the re-arrangement of the atoms.

Abel's theory was examined experimentally by Champion and Pellet.* They took a tube seven meters long, made in two lengths, and joined by a paper band. Small quantities of nitrogen iodide were placed in each end, and when one was exploded it immediately caused the explosion of the iodide at the other end, but, if the paper band connecting the two lengths was removed, this result was not produced. By a suitable apparatus it was shown that the effect produced was not due to the action of a puff of air, but to vibrations of the air such as are caused by a sounding body. When they attached nitrogen iodide to the strings of a double bass, and bowed the string, the iodide exploded when placed on the string giving the highest note, but not when on the two lower strings. The lowest number of vibrations which would cause explosion was found to be thirty per second. Similar results were obtained with other musical instruments.

A further set of experiments was made to determine the difference between the vibratory motion excited by various detonants, and thus to account for the differences in their ability to provoke, by means of the intervening air, the explosion of other detonants placed at a distance. A series of sensitive flames were arranged corresponding

*Comptes rendus 25, 110.

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with the complete scale of *G* major, and 0,03 grams of mercury fulminate and nitrogen iodide were exploded near them, The nitrogen iodide produced no effect; but the mercury fulminate excited the flames *a*, *c*, *e*, *f* and *g*. This showed that the vibrations excited by the two explosives were very different; and also that the vibrations excited by the mercury fulminate act on flames belonging to some notes of the scale, to the exclusion of others.

On exploding these bodies nearer the flames than in the former experiment, while the nitrogen iodide excited only flames corresponding with the higher notes of the scale, the mercury fulminate affected all of them. On exploding 20 grams of nitrogen iodide near the flames it excited all of them. In these experiments it was observed that acute sounds predominate in explosions.

They also took two conjugate parabolic mirrors, covered their surfaces with lamp-black so as to prevent the reflection and concentration of heat rays from them, placed them 2.5 meters apart, and distributed small masses of nitro-glycerine or of nitrogen iodide at different points along the line of foci. They then detonated a large drop of nitro-glycerine at one of the foci, and they observed that the substances placed in the conjugated foci detonated to the exclusion of the same substances when placed at the other points.

Abel* continued these investigations on the transmission of detonation by means of tubes, using explosive agents which were less highly susceptible, such as gun-cotton, dynamite, etc., and the results tended, in his opinion, to confirm his theory.

According to Berthelot† none of these experiments appear to be conclusive, and several of them seem even to be directly opposed to the theory which Abel has ad-

*Proc. Roy. Soc. 22, 160.

†Sur la force des matieres explosive 1, 117–132; 1883.

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vanced. He notes first that the characteristic feature of the given musical note which is capable of determining each variety of explosion has never been established. It is only below a certain note that the effects cease to be produced, while they take place by preference, whatever the explosive bodies may be, by the action of the most acute notes. But these effects cease to be produced at distances which are incomparably less than the resonance of the chords in unison, which goes to prove that the detonations are functions of the intensity of the mechanical action, rather than of the character of the determining vibration. Similarly, the detonation ceases to be produced when the weight of the detonating substance is too slight, and when in consequence the mechanical energy of the shock is much weakened. Nevertheless, the specific vibratory note which determines the explosions should always remain the same. For instance, cartridges filled with 75 percent dynamite cease to detonate when the capsule contains a weight of fulminate less than 0.2 gram, the detonation only being assured in all cases by the regulation weight of one gram. This confirms the existence of a direct relation between the character of the detonation and the intensity of the shock produced by one and the same detonating substance as stated.

If it be true that gun-cotton will cause nitro-glycerine to detonate in consequence of the synchronism of the vibration communicated, then we do not understand why the reciprocal action does not take place; while the absence of reciprocity may be easily explained by that difference in the structure of the two substances which plays so important a part in the transformation of the mechanical energy into work. This diversity of structure and the modifications which it causes in the transmission of the phenomena of the shock and the transformation of

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the mechanical energy into thermal energy, may be cited to explain the facts observed by Abel.

The difference between the energy of pure fulminate and of fulminate mixed with potassium chlorate, which has been noted, is no less easily explained; the shock produced by the first body being sharper on account of the absence of all dissociation of the product (which is carbon monoxide), should be contrasted with the second case, where carbon dioxide is formed and dissociated. Perhaps, also, the formation of potassium chloride, which is disseminated through the gas produced, with the concurrence of potassium chlorate, weakens the shock, just as the silicon does in the case of dynamite.

All the effects observed with nitrogen iodide may be explained by the vibration of the supports and by the effects of rubbing which results therefrom, this substance being particularly sensitive to friction. The experiment with the conjugate mirrors may also be easily explained by the concentration in the focus of the movements of the air, and therefore of the mechanical effects which result.

Besides, M. Lambert has proved by experiments made for the Commission on Explosive Substances, that in the explosion of dynamite cartridges in tubes of cast iron of large diameter, regarded from the standpoint of detonations by influence, there does not appear to be any difference between the ventral segments and the nodes characteristic of the tube.

To clear up this matter by eliminating the influence of the supports and the diversity existing in the cohesion and physical structure of the solid explosive substances used, Berthelot undertook a series of experiments on the the chemical stability of matter in sonorous vibration, and especially on that of gaseous bodies such as ozone and

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hydrogen arsenide, or liquids such as hydrogen peroxide and persulphuric acid, all of these bodies being selected from among those which decompose with the disengagement of heat, precisely as explosive substances do. The experiments were made by enclosing the substances in glass vessels which were attached to one arm of a tuning fork which vibrated at the rate of 100 single vibrations per second, or by enclosing them in a glass tube which, by means of a rubber, was made to give 7200 single vibrations per second. The substances were analyzed before the experiments began, then subjected to the vibratory action for periods varying from one-half hour to one hour and a half, and again analyzed to determine the extent of decomposition. In no case was there any notable decomposition, and these results lead to the conclusion that endothermous substances are stable under the influence of sound waves, while they are decomposed under the influence of ethereal vibrations. The diversity in the mode of action of the two classes of vibrations is not surprising when we consider that the most acute sonorous vibrations are incomparably slower than the luminous or thermal vibrations.

From the consideration of the facts cited, and especially from experiments made in firing under water, Berthelot concludes that explosions by influence, like detonations in contact, are due to the transmission of a shock, arising from the enormous and sudden pressures produced by the nitro-glycerine or gun-cotton, which is converted into heat within the explosive material.

Thus, in the extremely rapid reaction which obtains, the pressures produced may approach to the limit which corresponds to the matter detonating in its own volume, and the commotion due to this sudden development of almost theoretical pressures can be propagated through the

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ground and supports as intermediaries, or through the air itself, being projected *en masse*, as has been shown in the explosion of certain powder factories and gun-cotton magazines, and in some of the experiments made with dynamite and compressed gun-cotton. The intensity of the shock propagated either by a column of air or by a liquid or solid mass varies with the nature of the explosive body and its mode of inflammation; it is of greater violence according as the duration of the chemical reaction is shorter and develops more gas, that is to say, a higher initial pressure, and more heat, and consequently work, for the same weight of explosive material.

This shock is transmitted better by solids than by liquids, better by liquids than by gases; with gases it is better as they are more compressed. Through solids it is better propagated according to their degree of hardness, iron transmitting it better than earth, and hard ground better than ploughed soil. All breaks of continuity in the transmitting material tend to weaken it, especially if a softer substance is interposed. Thus it is that the use of a tube made from a goose-quill, as a receiver, stops the effect of mercury fulminate, while a tube or a capsule of copper transmits this effect in all its intensity. Explosion by influence is the better propagated in a series of cartridges according as the envelope of the first detonating cartridge is the more resisting, as it thus enables the gases to obtain a greater pressure before the covering is destroyed. The existence of an empty space, that is to say, one filled only with air, between the fulminate and the dynamite, diminishes the violence of the shock transmitted, and in consequence that of the explosion, and in general the effects of violent powders are lessened when there is no contact. To form a full conception of the transmission by the medium of

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sudden pressures which produce shock, it is desirable to recall the general principle, in virtue of which pressures are transmitted in a homogeneous mass equally in all directions, and are the same on any small element of the surface whatever its position. Detonations produced under water with gun-cotton show that this principle is equally applicable to the sudden pressures which produce explosive phenomena. But it ceases to be true when one passes from one medium to another.

If the inert chemical matter which transmits the explosive movement is fixed in a given situation like the surface of the ground, or better still, held by the pressure of a mass of deep water, in the midst of which the first detonation is produced, the propagation of the movement in this medium will hardly be able to take place, except under the form of a wave of a purely physical order, and consequently of an essentially different character from the original wave which is developed in the explosive body itself, and which is of a chemical and physical order. Whilst the first wave, which is of a chemical order, is propagated with a constant intensity, this new wave, which is of a physical order, transmits the concussion away from the explosive center all around it, with an intensity which decreases inversely as the square of the distance. In the neighborhood of the center of the explosion the displacements of the molecules may overcome the cohesion of the mass and disperse it, or crush it by enlarging the explosion chamber, if the operation is conducted in a cavity. But at a very short distance (the magnitude of which depends on the elasticity of the surrounding medium) these movements, confused at the beginning, arrange themselves in such order as to produce a wave, properly so called, characterized by compressions and sudden deformations of the mater-

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ial, the amplitude of these oscillations depending upon the magnitude of the initial impulse. They move with a very great rapidity, and preserve their irregularity up to the point where the continuity of the medium is interrupted; then these compressions and sudden deformations change their nature and are transformed into a movement of impulse, that is to say, they reproduce the shock. If then they act on a new cartridge they may determine its explosion; the shock will be otherwise weakened by the distance, and in consequence the character of the explosion may be modified. The effects diminish in this manner up to a certain point from which the explosion ceases to produce itself. When this occurs with a second cartridge the same series of effects will be continued from the second to the third cartridge; but this depends on the character of the explosion which the second cartridge undergoes. And thus it goes on.

Such is the theory that Berthelot offers to explain explosions by influence and the phenomena which accompany them. It depends, definitely, on the production of two orders of waves: one series representing the explosive waves, properly so called, developed in the midst of the matter which detonates, and consisting of a continually reproduced transformation of chemical actions into thermal and mechanical actions, which transmit the shock to the support and to the contiguous bodies; the other being a purely mechanical and physical series, which transmits the sudden pressure equally about all the center of the concussion to the adjoining bodies, and by a singular circumstance to a new mass of explosive material.

As to the action within the original mass he holds that the kinetic energy of the shock of the explosion (by the detonator) is transformed into heat at the point struck; the temperature of this point is thus raised to the tem-

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perature of explosion; a new shock is thus produced which raises the temperature of the neighboring portions to the same degree; they then explode and the action is propagated with an ever increasing velocity.

Neither Abel's theory of synchronous vibrations nor Berthelot's theory of explosions by influence satisfy Threlfall*, and he hence has made an experimental and critical study of the manner in which the explosive reaction is communicated from one explosive mass to another explosive mass through a non-explosive medium. Much might be learned from a measurement of the velocity of transmission of a shock to points at small distances from the center of explosion. This would be merely a question of apparatus, and Lord Rayleigh suggested the use of a sensitive flame and revolving mirror, which would, at all events, give some idea of the sort of disturbance experienced; but Threlfall deemed it best to begin by examining cases where the results of explosion could be seen and watched.

For this purpose he constructed a tank measuring a yard each way, and provided with windows in the sides. The tank was filled with water, and water-tight glass bulbs of $\frac{1}{2}$ inch diameter, filled with mercury fulminate, were sunk to the depth of 18 inches in the water, fired by electricity, and the course of the *debris* from the explosion noted. As the torpedo was suspended vertically, this *debris* had the appearance of being shot down to the bottom of the tank — not in a jet, as might have been expected, but with exactly the rolling motion that smoke has in coming out of a chimney — as if, in fact, there was vortex motion of some sort. The constancy of the downward action of the explosion suggested that it was due to the want of symmetry introduced by the neck

*Phil. Mag. 21, 164–180; 1886.

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and wires of the torpedo. Hence experiments were made in which the torpedoes were placed horizontally, and then the *debris* seemed to move, with its peculiar rolling motion, horizontally away from the neck. In fact, the appearance presented to the unaided eye was that of a more or less definite column of rolling white smoke shot out with great velocity, and coming to rest very rapidly when about five inches from the center, as if acted upon with an irresistible force. Experiments were also made by exploding a charge in the center of a Florence oil flask filled with red dye and immersed in the water. The dye was shot out with the *debris*, and the flash appeared to be suddenly stopped some two or three inches outside where the flask would have been if it had not disappeared. There were, however, so many sources of misinterpretation to be feared in this method of observation that it was not continued, but the experimenter contented himself with noting the peculiar rolling and the dead-beat motion of the dye as it was shot out.

Experiments were now made to determine if the directions of projection of the *debris* coincided with the directions of propagation of the streams of explosive energy. For this purpose a pendulum gauge was devised which was fitted to the tank, and by firing some dozen torpedoes arranged as symmetrically as possible, he found that the indications of the gauges were nearly proportional. Explosions were then produced in torpedoes purposely made unsymmetrical, either by having the glass too thick on one side, or by turning up the ends of the covered conducting wires so that they entered the bulb horizontally and facing one of the gauges. The effects now became more puzzling, but on the whole there was no question but that the gauge towards which the bulb was turned suffered most. In fact, the direction taken

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by the streams of explosive energy appeared to coincide with the directions of projection of *debris*, and with the direction foretold from the initial conditions.

The experiments were repeated at various distances and in various manners with more or less compressed charges, and with variations in the position of the firing-point. The pendulum readings were on the whole certainly proportional to the direction of explosion as foretold from the initial conditions. Of course in some few cases there were unexpected actions on the gauges; but this was hardly avoidable, since the previous experiments had shown how small a change in initial conditions could lead to great variations in the result. The position of the firing-point was the least satisfactory part of the experiments; most of the failures could be traced to imperfect centering of the firing-point; about ten percent of the experiments failed to travel on the paths laid out for them. These experiments leave little doubt that the direction in which the maximum explosive effect is transmitted will in a great measure depend on the initial arrangement of surrounding obstacles;* at all events, when the explosion is caused by fulminate of mercury and small charges are used.

In fact, the shock of an explosion must be transmitted in one or more of three different ways:

I. By actual bodily motion of the products of explosion through the surrounding medium, either alone or becoming more and more mixed up with the medium itself, which is thereby set in motion.

II. By an undulatory motion set up in the medium.

III. By vortex-ring motion.

In the explosion of gunpowder and other slow explosives the energy is transmitted chiefly by I and II. The

Proc. Nav. Inst. 9, 735; 1883.

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distance to which a considerable quantity of the energy may be conveyed by means of waves of comparatively great amplitude is in some cases remarkably great. This is evidenced by the effects produced by the explosion of powder magazines.

In the case of the fulminates of mercury and silver, gun cotton and nitro-glycerine — that is, explosives of the class examined under water — the effect falls off very rapidly with the distance, and in water, at all events, is of a directed character. This would point to the third mode of transmission being in these cases of some importance; and if we consider the way in which the products of explosion escape, we shall find that the conditions for the production of vortex motion do exist. Let there be a sphere of mercury fulminate fired from its geometrical center. Then, by Vieille's* experiments on the time of explosion, it seems likely that the outer portions of fulminate will be decomposed before they are removed to any appreciable distance from their original positions. We shall therefore have a sudden expansion in all directions, caused by the increase in volume of the explosive substance during the explosion. There seems no reason, why, under perfectly symmetrical conditions, the expansion should not go on as it began until the cooling of the sphere of hot gases becomes so marked as to prevent further expansion.

If the conditions, however, are not such as to allow of symmetrical expansion — which occurs in practice — then we shall have the bounding surface of the explosion gases more curved in some places than in others; that is, the strain will be greater at some parts than at others, and in fact may become so great at points of greatest curvatures as to lead to a state of "breakdown." In other

Compt. rendus 1882 and 1883.

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words, the compressed gases in this case escape, not by gradual expansion, but by jets, from points whose positions are fixed by the conditions of explosion. In these jets we should have the necessary and sufficient conditions for the establishment of vortex motion. If vortex motion were set up, then it seems likely that much greater effects might be transmitted in some directions than in others, though at considerable distances the effects would tend to become uniform in all directions.

Threlfall believes that this view of the actions of explosions will enable us to explain several difficulties occurring in the interpretation of Abel's experiments. Among these are: The want of correspondence between the explosive actions, as measured by the effect produced on copper plates, and the effects produced in causing other explosions; the apparent capriciousness of explosions of the more violent kinds; the production of explosions by influence.

In his discussion of explosions, Berthelot has not added anything to the generally accepted theory that the explosion of gunpowder differs in no way from ordinary combustion, except that it is more rapid. His theory of detonation, however, is novel and many experiments tend to show the justness of his views. To begin with, Abel found that almost any variety of effect could be obtained by burning explosives under diminished pressure. For, the lower the pressure, the more easily do the products of decomposition escape and carry with them the energy due to their liberation. By this means the temperature of explosion is constantly kept down, and the chemical character of the products modified in such a way that they correspond to the temperature. In other words, the compounds liberated are, as a rule, more

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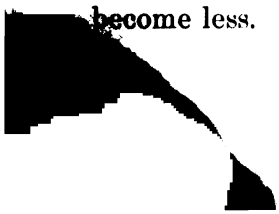
complex than those which would be set free at a higher temperature, and therefore the energy run down is less.

Again, it will come to the same thing, so far as the propagation of an explosion is concerned, whether the products of decomposition are facilitated in their escape by conducting the experiment in a partial vacuum, or whether the decomposition is itself so slow that the products are enabled to escape without marked hindrance under ordinary pressure. Now, the resistance of the air to the escape of the products of combustion will depend on the rate at which they are liberated. And the shock given to neighboring portions of the explosive will be proportional to the pressure of the explosion gases at these points, and therefore ultimately to the resistance of the air, and hence to some function of the velocity of decomposition. But, in order to convert an explosion by combustion into an explosion by detonation, what is required is that the temperature of any point shall be raised sufficiently to determine its complete, as distinguished from its incomplete, decomposition. The raising of the temperature of any point, however, will depend on the violence of the shock to which it is subjected; and this, as before stated, will be proportional to some function of the velocity of the decomposition producing it. If the necessary temperature is anywhere attained, we shall have detonation thereafter; if not, an explosion by combustion will result. It appears, therefore, that in order to produce a detonation, we require the initial velocity of decomposition to rise above a certain minimum value—that there is, in fact, a "critical velocity" of initial decomposition which determines the kind of reaction that ultimately takes place. If the temperature of the whole mass be previously raised, then the critical velocity will become less. Berthelot considers that a specific change



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takes place in the stability of an explosive as its temperature is raised. This is doubtless true; but if a minimum temperature of any part be the necessary and sufficient condition for the production of a detonation, then the ease with which it can be obtained, when the mass starts with a high temperature, will, *cæteris paribus*, be greater than if the original temperature is low. If, therefore, we find that nitro-glycerine is more liable to detonation the higher its initial temperature, we shall not be required to make any assumption as to "increased sensitiveness," since we see that the minimum temperature will be more easily reached, and that therefore the critical velocity of initial decomposition may be smaller. In other words, supposing we try to detonate nitro-glycerine by an explosive which just fails at ordinary temperatures, we should expect its chances of success to increase as the temperatures rises; and this does, in fact, occur.

The sensitiveness of an explosive to detonation has been found to depend on its state of aggregation. The critical velocity required to produce detonation will, *cæteris paribus*, depend on the nature and value of the elastic constants of the explosive, as well as of the medium in which it is to be exploded. We should, in fact, expect a change in the critical velocity of detonation if we exchanged the viscous resistance of liquid nitro-glycerine for the elastic resistance of the same substance when frozen. Again, it seems possible, as a result of this theory, that less powerful detonation might be required to explode a given substance in water than in air; but the author is not aware of any experiments on this point. And so in other cases, though the critical velocity of detonation must necessarily be a very complex function, and difficult to predict; yet there appears to be no reason on that account to minimize its importance. On

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the other hand, it seems to the author to be in complete harmony with Abel's experiments, and substantially embodies the views set forth by Dixon,* and the author knows of not a single experiment which offers any evidence against it. What is required by the theory for the production of a detonation is that a small part of the mass should be raised above a given temperature, and not that a large portion should be raised to a temperature below it.

This leads at once to the consideration of the second point—viz: the action of detonators. The apparently anomalous effects discovered by Abel may be summed up by taking the most extreme case. Gun-cotton could be detonated by a charge of fulminate of mercury, whereas ten times as much nitro-glycerine was required to cause a similar sample of gun-cotton to detonate. By firing the detonating charges on copper plates, Abel naturally observed that the destruction produced by the nitro-glycerine was much the greater, and hence concluded that some other factor besides the "explosive violence" must come into play. This is undoubtedly true, but the mistake arises in looking at the experiments from one point of view alone—viz: that of the copper plate. There will be no effect produced on the plate at all till the resistance of the air becomes greater than that of the plate; and this will never be the case, however great the volume of gas liberated, unless the time of explosion be sufficiently short. The resistance of the air varies at least as the square of the velocity of attack, and therefore this will be the conditioning factor of the destructive effect producible by explosions in free air. For a given increment of volume occurring in an explosion, till the time of explosion diminishes to a certain

*On Conditions of Chemical Change in Gases, *Phil. Trans.*, 1884.

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value depending on the strength of the plate, no effect will be observed; directly this limit is passed, the destructive effect will depend in the usual manner on the quantity of energy liberated. There is, in fact, a critical velocity of explosion below which the plate will not be attacked. But in a detonation the case is different. We do not require any great destructive effects; we only require that the time should be so short that a portion, no matter how small, of the substance to be detonated should be raised to the appropriate temperature. If the detonator has a time of explosion too great, then, although the air may be the stronger obstacle and the explosive destroyed, no detonation will be produced. This is precisely what happened in Abel's experiments, when the gun-cotton was blown to pieces by the nitro-glycerine. The instantaneous rise of pressure is not so great for nitro-glycerine as for fulminate of mercury, though the energy run down is much greater. This point has been satisfactorily proved by Vieille in his experiments with the crusher gauge. Moreover, the density of mercury fulminate is three times that of nitro-glycerine, which allows a given mass to be on the whole much nearer its work if it consists of mercury fulminate, than if it consists of nitro-glycerine.

We ought not therefore to be surprised that the detonation of gun-cotton is easily accomplished by mercury fulminate, and hardly accomplished by nitro-glycerine. If there is any surprise, it would seem more fitting that it should be exhibited at the detonation which large charges of nitro-glycerine seem able to effect. This fact would tend to show merely that nitro-glycerine has a velocity very near the critical point for gun-cotton — so much so, that when large charges are employed the acceleration in the explosion of the nitro-glycerine is suffi-

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cient to pass the limit. We know from Dixon's work on gases that at first the explosion gains in velocity till the steady velocity of detonation is obtained, and there seems no reason against, but, on the other hand, every probability in favor of, the same thing taking place in nitro-glycerine.

Above and beyond this, the difference in the mode of application of the two detonators must be taken into account. In Abel's experiment the fulminate was enclosed in a tube of copper or tin plate, while the nitro-glycerine was merely applied in a capsule whose diameter was large compared with its depth. The upper end of the fulminate tube was probably closed by the electric firing-apparatus; and this, as was shown by the experiments in water already described, together with the fact that the fulminate was fired at the top, would give it an enormous advantage. For there is considerable probability that in explosions of high velocity in air, the final mode of "breakdown" of the gas liberated is very dependent on the initial conditions, just as it is shown to be in water. The nitro-glycerine was deprived by Abel of these advantages; and for these and the reasons above mentioned, though it was able to blow blocks of compressed gun-cotton into powder, and even to cause some of this powder to penetrate the hard wood of the support, it failed to cause detonation.

The other apparently anomalous facts observed by Abel require further treatment, and, most of all, those explosions by influence, which seem at first sight only explicable by some theory such as that of synchronous vibrations. The first set of experiments bearing on this hypothesis have been already discussed, with the result that the hypothesis is perhaps unnecessary. There are, however, a great number of other experiments, some of

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which cannot be so easily explained. In the experiments made with tubes the great influence exerted on the detonating power by the smoothness or roughness of the walls of the tube seem a strong argument against the supposed synchronism having much to do with the effect in these cases. In fact, it is just what we should expect if there was bodily motion down the tube, or even if, as in the case where diaphragms were inserted, the motion was transmitted from layer to layer without any great amount of displacement in each individual particle. It seems possible that some vortex motion caused by the "breakdown" might be transmitted through the tube, and that the diaphragms merely served to change the portions of air of which the rings were actually composed. Threlfall admits that this is not very satisfactory; but if the roughening of the internal surface of the tubes actually exerted the effect attributed to it, we are justified, in his opinion, in supposing that the explosions were not caused by the transmission of vibrations through the material of the pipe itself. Again, vibrations, to be of any effect in producing chemical change, must be comparable as to period with the molecular vibrations. If such vibrations are transmitted through ether, it is difficult to see where the influence of chalking the inside of the tubes can come in; and if through air, their wavelength would be too small (as will be shown) to be likely to be much influenced by particles of the size of chalk-dust.

The similar experiments of Champion and Pellet* are sufficiently explained by their statement that they used nitrogen iodide. Unless any one likes to suppose that the period of a fiddle-string may be comparable with the period of a nitrogen iodide molecule, the further experi-

*Comptes rendus 75, 110.

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ments of Champion and Pellet cannot be held to have much bearing on the subject. One can only wonder that they found a string that would vibrate slowly enough not to fire their iodide. As to their experiments with mirrors, blackened or otherwise, the results obtained might be anticipated on almost any theory except that of "synchronous vibrations." For the vibrations supposed on this theory to be most active would be precisely those absorbable by lampblack. This point has been investigated by Berthelot in a manner which leaves little doubt that he misunderstood Abel's theory, when, in order to show the importance of vibrations in producing chemical change, he experimented on various chemicals by swinging them on tuning-forks. No effect was produced, nor indeed was it to be expected, unless the reagents were of such a nature that they required intense shaking to keep them mixed. Berthelot's results with the vibrating tube is very interesting, but does not seem to touch Abel's theory. In order to disprove the theory, Berthelot ought to have made his tube vibrate till it got luminous, and observed the effect on the ozone all the way up.

There are many well-established cases of torpedoes exploding one another by influence, and the same thing occurs in firing dynamite shots in mines. The former alone possesses any interest for our present purpose. If the effects due to mercury fulminate, when fired under water, are in any way similar to those which may be supposed to take place on the detonation of large charges of gun-cotton, then, by the experiments described above, it would be likely that quite extraordinary effects might be propagated in some cases. There ought, however, to be a capriciousness in the observed action of torpedoes on one another; whether this has been observed or not, the author is unable to state, but he assumes that it has

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not, and that here we may have a case where the effect is largely due to "synchronous vibration." He therefore considers the ways in which vibrations of sufficiently small period could be transmitted, first assuming that no vibrations can have any influence unless they are of such period as to be comparable with the natural period of vibration of the molecules of the substance to be exploded.

Let a body be gradually heated, and its temperature measured as soon as light comes from it having the same refrangibility as the line *A* in the solar spectrum. Let the temperature be, say, of the order of 1500° C. Then the molecules of the body will be vibrating in some way comparable with the period of the *A* line; that is, about 4×10^{14} times per second. Suppose gun-cotton could be heated red hot without decomposition; then its molecular period would be of this order. We are quite unable to say how the period varies with the temperature in solid bodies at low temperatures. But the spectroscope shows that it does not change much at high temperatures.

The only possible way of obtaining an idea would be to extend the spectroscopic investigation even further than it has been done by Abney; either photographically or by the thermopile. We will assume, however, that as the bodies cool, their molecular vibrations, if altering at all as to period, tend to become slower, as well as of smaller amplitude. Let us consider the limiting condition of propagation of waves of longitudinal displacement. There seems no reason for supposing that the velocity of propagation would fall off till we come to waves of a wavelength comparable with molecular distances — for instance with the mean free path. Now, by experiments in diffusion, it seems that the mean free path in oxygen is of the order of 5.6×10^{-6} cm.; in sugar solution it is 10^{-5} of this, or 5.6×10^{-11} cm.; while in solids it is probably

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much less. The size of the molecule, however, seems to be of the order 5.8×10^{-8} cm., so this will give our superior limit in solids and liquids.

Suppose that the smallest wave-length is the diameter of a molecule, and that the velocity of propagation is the same as that of sound down to this limit. Then if V be the velocity of propagation, or the number of vibrations per second, and λ the wave-length in water, we have

$$n = \frac{V}{\lambda} = \frac{1.4 \times 10^5}{5.8 \times 10^{-8}} = 2.4 \times 10^{12}.$$

But it is unlikely that we could get a wave-length anything like so small as this, so let us take as our limiting value the wave-length equal to a thousand molecular diameters. This gives us for the limiting frequency

$$n = 2.4 \times 10^9.$$

Comparing this with n for the A line, which is 4×10^{14}, we see that it is about a million times too slow to produce any effect on molecules vibrating so as to emit red light. But bodies at the ordinary temperature might possibly vibrate slowly enough to be influenced directly, though this is unlikely. It is rather surprising that the numbers are as comparable as they seem to be. If we perform the same operation for gases, putting $\lambda = 1000$ mean free paths, we get for oxygen $n = 5 \times 10^6$. Here the discrepancy is a thousand times as great; so that if longitudinal vibrations are to be considered as likely to produce any effect, they will be considerably more likely to do so if transmitted through solids or liquids than through gases. We have still got the ether to fall back on, and there we are safe, for there is no reason why vibrations of the right period should not be transmitted through it.

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The experiments with tubes, however, seem to point exclusively to the air as the medium through which vibrations are to be transmitted, and that may be fairly regarded as unlikely. If the synchronous vibrations can be disproved at all by experiment, then Abel has, at all events, made the most telling experiment against it; there may, of course, be other experiments, and these may point in the opposite direction, but the author has failed to learn of them. Still, in the light of what has been published on the subject, there is little doubt that our natural hesitation to accept a theory of vibrations is justified by a consideration of the facts. On the other hand, if we admit that vortex motion may exist, it will account for some of the effects observed in the neighborhood of violent explosions. The most important effect to be accounted for is the capriciousness of explosions. Instances are so numerous that it is hardly worth while to dwell upon them in detail; but take the famous explosion at Bremerhaven, for instance, and it is curious to note the way in which the bystanders seemed actually singled out for injury, and that not always from flying *debris*. Such effects as these are difficult to account for on any theory of uniform propagation of wave-motion. On the other hand, any of the observed phenomena of propagation of explosion are as well explained by vortex propagation as by wave motion. There is no reason why the two states of propagation should not exist together, varying in their relative importance according as the explosion is of long or short duration. In ordinary cases of detonation, we may imagine the shocks to be given by the explosion gases before any considerable breakdown has taken place.

Reference books, *Hill's Notes, Proc. Naval Institute, Berthelot's Sur la force des matieres explosives.*

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LECTURE XII.

THE USE OF HIGH EXPLOSIVES IN SHELL.

The use of high explosives in shell, although first attempted more than twenty years ago, is still in the experimental stage, chiefly owing to the difficulty of regulating the time of explosion. When this has been accomplished, certain advantages will result. For field guns these advantages will chiefly come from thicker and heavier shell, broken into more numerous and regular fragments, and available for longer ranges than at present. For medium calibres, such as are used in sieges and bombardments, the shell capacity is necessarily too small to carry decisive charges for this use, and the effects will be moral rather than physical. This is due to the intensely local action of these high explosives. The terrifying sound and frightful effect upon the object struck will perhaps appal new men, but old sailors will soon learn that the danger is overestimated. These calibres may also come into play for defense against boats and in countermining. For the much larger calibres it is stoutly claimed that charges of size to be destructive in themselves may be employed even against armored ships, either in armor-piercing shell, or else in steel or other highly-resisting envelopes, by which the projectiles may

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be made to serve the purpose of aerial torpedoes. It is possible, also, that with such shell charges the older forms of ordnance may be rendered so efficient as to still prove useful. As the experiments which are being made in this direction are now exciting much interest, a brief resume of what has been done may not be unacceptable.

In 1864 the English Gun-Cotton Committee* fired twenty-five rounds with unfused shell filled with dry, long, staple gun-cotton. Ten rounds were fired from the 10-inch smooth bore. The shell weighed 79 pounds, had a capacity for 6¼ pounds of powder, and were fired with a charge of 12 pounds, which imparted 1292 foot-seconds initial velocity. The shell were loaded with from 11 ounces to 1 pound, 12½ ounces of unsilicated gun-cotton, eight of them being packed tightly and the other two loosely. All were fired without bursting.

Ten rounds were then fired from the 13-inch mortar. The shell weighed 194 pounds, had a capacity for 10½ pounds of powder, and were fired with a charge of 20 pounds, which imparted 905 f. s. initial velocity. The shell were loaded with from 1 pound, 11½ ounces to 2 pounds, 15½ ounces of gun-cotton, the cotton being unsilicated in the first six rounds, and silicated in the remainder. All were fired without bursting.

Five rounds were fired with the 7-inch B. L. Armstrong. The shell were elongated, being 18¾ inches long, weighed 98 pounds, had a capacity of 8 pounds of powder, and were fired with a charge of 12 pounds, which imparted 1172 f. s. initial velocity. The shell were loaded with from 2 pounds to 2 pounds, 8 ounces of unsilicated gun-cotton. The shell did not burst in the first, third and fourth rounds. In the second it burst just beyond the muzzle, and in the fifth it burst within the bore and

Rept. Gun-Cotton Committee, 1864-1868; London, 1869.

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damaged the gun so as to make it apparently unfit for service. It was believed that these explosions were due to the compression or friction produced by the "setting up" of the comparatively loose charges at the moment of starting.

In 1867 experiments were resumed with compressed pulped gun-cotton, the explosive being in 3½-inch discs, about 1 inch thick, made under a pressure of 6 tons per square inch. The shells used were of steel, with heads which could be unscrewed so as to throw open the whole interior space. The shell were filled as compactly as possible with discs, the sides being protected by thick brown-paper coatings, and the vacant spaces at top and bottom being filled up by brown paper and sugar, so as to prevent (apparently) any possibility of friction or motion. Precautions were taken to guard against the flame from the ignited cartridge penetrating through the screw-threads. Two rounds were fired from the 8-inch shunt gun. The shell weighed (empty) 144 pounds, carried a charge of 3 pounds, 2 ounces of gun-cotton, and were fired with 30 pounds of powder, which imparted 1320 f. s. initial velocity. In the first round the shell burst after one graze on the range. In the second the shell burst in the bore shattering the chase and leaving nothing in front of the trunnions.

One round was fired from the 7-inch M. L. Woolwich. The shell weighed (empty) 112 pounds, carried a charge of 2 pounds, 8 ounces of gun-cotton, and was fired with 22 pounds of powder, which imparted 1465 f. s. initial velocity. The shell burst inside the bore, and the gun was cracked and expanded but remained entire.

We have no further record of English experiments in this direction, but, according to Abbot,* they have suc-

*Proc. Nav. Inst. 11, 765; 1885.

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ceeded better with wet gun-cotton, and they claim to have realized safety in firing and to possess a good arrangement for effecting the explosion after impact, and from the rumors which reach us from Lydd and from the experiments on the Resistance, there seems to be little doubt that gun-cotton is proving its efficiency.

According to Hill,* experiments were successfully carried out, before 1875, on a plan suggested by Prof. Abel for employing it as a bursting charge, in what are known as "water shells"; that is, shells containing small charges of a high explosive and having the remaining space filled with water. Owing to the incompressibility and high elasticity of the water, the energy developed by the explosive is immediately communicated to the walls of the envelope and ruptures it. This is well shown by means of a Prince Rupert's drop in a flask of water.

In these experiments 16-pounder shell were tried, in which a 1-ounce or ½-ounce disc of dry gun-cotton, with a 15-gram mercury fulminate detonator attached to an ordinary percussion fuse was placed, and the remaining space filled with water. The conclusions were that the shell prepared as described could be safely fired from field guns, and were more efficient than when charged with gun-powder. Experiments were also tried with 9-inch shell containing as much as 10 to 12 pounds of wet gun-cotton with a dry priming charge arranged as above described. Very good results were also obtained in practice against targets representing troops.

In 1882 the German artillery began† experiments on the use of gun-cotton for shell. These experiments were made primarily in order to determine the possibility of using large charges in projectiles for the 21-cm. mortar. For this they used cast-steel projectiles, with thin

*Notes on Explosives 47; 1875.

†Revue d'artillerie 29, 536; 1886.

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walls, which were five calibres in length. Apparently they met with success, for they have adopted torpedo shell for this mortar which are made in two parts, a body and a head, screwed together. The charge is enclosed in a zinc or iron box, and is composed of discs of compressed gun-cotton 5 cm. thick and containing twenty percent of water. The upper disc carries a cylindrical cavity which holds a primer of dry gun-cotton, and the latter is pierced with a detonator hole. When the charge is placed in the box a rod of wood is inserted in the detonator hole, and melted paraffine is poured in to fill the interstices between the discs. The box is closed with a metal cover pierced with a hole for the detonator. When the box is introduced into the shell the head of the latter is screwed on, and a hollow screw is inserted in the eye of the shell in order to hold the box in place, and at the last moment the fuse and detonator are inserted in the aperture in the screw. The use of discs admits of greater density of loading, the charge being about four times as great as when granulated gun-cotton is used; but, on the other hand, it requires that the projectile should be in two parts, and that special discs should be made for each caliber.

These projectiles have given good satisfaction, not only in the 21-cm. mortar, but also in the 15-cm. and the 28-cm. In the latter piece the shell is loaded with fifty kilo. (110 pounds) of gun-cotton.

It appears probable from the above that the method of forming and charging these shell is a late invention, as it is so similar to the one ascribed farther on to Von Forster and Wolff.

In August, 1884, Comdr. Folger, U.S.N., fired 15 rounds of gun-cotton at a range of 2000 yards with the 80-pounder (6.4 inch) B. L. R., using full service charges of powder

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(10 pounds) and shell filled with gun-cotton saturated with water (3 pounds). The only precaution taken to relieve the shock at starting was in placing a layer of oakum $\frac{1}{4}$ inch thick in the bottom of the shell. Three shell were also fired at an iron target, 50 yards distant, with a velocity of impact of about 1250 f. s. There was no premature explosion in any case. It should be said that though service gun-cotton was used in these experiments the discs were broken up in order to feed them through the fuse hole, and that the density was consequently much reduced.

In 1883 Messrs. Von Forster and Wolff† took out two patents — one for a process for preserving gun-cotton, the other for the construction of a shell charged with this explosive. The process of preservation invented by Von Forster consists in plunging the gun-cotton, wet or dry, into ether for 15 or 20 seconds; there is formed on the surface a very thin, hard layer impermeable to water and of a yellowish-brown color, thus giving the gun-cotton the appearance of wood. Nitro-benzene or other liquid solvents of gun-cotton may be employed in place of the ether. This layer does not effect the explosive properties of the substance, but diminishes loss by flaking and cleavage, retards decomposition, maintains the humidity at nearly the desired point, and prevents the penetration of paraffine. However, this pellicle contains always some very small interstices through which moisture may escape eventually, but this imperfection may be neglected if the gun-cotton is properly stored. Gun-cotton, not coated and containing 25 percent of water, looses all its water in a few days if it be exposed in a brisk current of air, while the coated gun-cotton, exposed under the same circumstances, is not reduced to the dry state in as many weeks. Besides, the layer is so thin that its combustibil-

*Revue d'artillerie 29, 530—536; 1886.

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ity does not constitute a source of danger. In the case of dry gun-cotton for use as primers, after the treatment with ether, the detonator canal is plugged with paper and the disc is dipped in melted paraffine. This forms a second impermeable varnish.

The projectile described by the second patent is of cast iron formed of two parts which screw together, the interior being filled with discs of compressed gun-cotton. At the base of the shell is a fuse which fits into the perforations in the discs. The shell is provided with an ordinary percussion fuse, and this is connected with the primer by a fuse composition, which may be either gun-cotton in fine grains or a mixture of this body with meal powder. The patent does not state how the fuse is held in place.

The arrangements described have been chosen as the result of experiments made at Walsrode on the effect of the explosion of gun-cotton in free air. These experiments of M. von Forster's led to the following conclusions: the power of gun-cotton increases with the density; in the moist state it is more *brisant* than when dry; it is advantageous to produce the inflammation of the charge at the part furthest removed from the object to be destroyed; and, finally, a cavity so placed as to follow the axis of the charge favors its action.

It does not appear that the shell described above has been experimented with, and later experiments on the explosion of gun-cotton in free air do not appear to confirm the conclusions reached relative to the position of the fuse and the existence of the central canal. They have, however, sought to utilize existing projectiles by devising means for charging them through the eye of the shell. These efforts led to the taking out of another patent in May, 1885, for a method of charging and for a special mode of fixing the detonator.

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The gun-cotton is used in the form of prismatic grains obtained by breaking up the compressed discs. They place 200 grams of dry gun-cotton upon the charge of wet gun-cotton. When the charge is in place they introduce a mandrel through the eye of the shell, thus forming a canal in the cotton for the detonator and fuse, and they pour into this space melted paraffine having a temperature of 75° to 80° C. This paraffine fills all the interstices between the grains, and in solidifying binds them into one compact mass. The fuse is similar to the German percussion fuse, model of 1873. The plug is elongated and opened at its lower end; it encloses a capsule containing one gram of fulminating mercury, and is surrounded by a band and tube, both of caoutchouc. The whole arrangement is held in place by a screw. If they wish to obtain a retarded effect they use a longer plug and interpose a fuse composition between the exploder and the detonator. In order to assure intimate contact between the fulminate and the charge they place a 10-grm. disc of dry gun-cotton around the detonator, and protect it from the action of shocks by caoutchouc bands.

The shell are charged before being stored in the magazine, but the detonators and fuses are put in place at the time of firing. A brass tube, designed to receive the detonator, protects the charge up to this time.

In the spring of 1885 the German Government furnished the Walsrode factory with a 15-cm. gun for the trial of this mode of charging. They used lead-covered shells of 2.5 cal. model of 1869, weighing 27 kg. and having a capacity of about 2 dm^3. Each shell received a charge of 1.35 kilo. of gun-cotton, with 20 percent of water, in parallelopipedons 10 mm. on the side and 20 mm. long, and 200 grams of dry gun-cotton in cubical grains of 6 mm. on the side. They fired the charge of

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1.5 kg. against a parapet situated at a distance of 70 m. The velocity, measured at 30 m. from the muzzle, was 245 m. Out of five projectiles no premature explosion was obtained. Two of them had been fitted with retarded fuses, and these produced deeper craters than the other three. The number of fragments was considerable, and their dimensions did not surpass some millimeters. A shower of fragments were thrown more than 70 m. to the rear.

They exploded a shell buried 1 m. in the earth and obtained a circular crater about 2 m. in diameter, 70 cm. deep, and of a capacity of 1.25 m^3.

M. von Forster replaced this method adopted for holding the detonator by another, which is not described, but which seems to have given good results. He pursued these experiments and proved successively all the elements of the proposed system. For this purpose he fired an empty shell furnished with an unprimed fuse, and with damp gun-cotton in the detonator, and he found that the fulminate in the capsule was not exploded. Then loaded shells containing neither fuse nor capsule were fired. There was no explosion and the gun-cotton was recovered unchanged. Next loaded shells, fused but not primed, were fired with a velocity of 420 m. against a parapet of wood, and afterwards of iron. There was no explosion, but as the resistance was increased the shells were broken up as if empty, and sometimes, though not always, the gun-cotton was set on fire.

Finally, he experimented with shell completely charged, fused and primed. More than 200 projectiles of 8.8 cm. were fired with a velocity of 450 m. The ordinary shell charged with gun-cotton were thrown from the rifled 15-cm. mortar with a velocity of 200 m., and from the 15-cm. gun with a velocity of 400 m. These last two

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pieces also projected steel shell of 6 calibers charged on the same system. There was no case of breaking up in the gun, and the final explosion was always complete.

In the experiments in breaking up at rest they have counted for a cast-iron 8.8-cm shell, weighing seven kilo., 200 fragments weighing over ten grams each, and 600 weighing from one to ten grams. An 8.8-cm. steel shell weighing 6.64 kilo. gave twenty-three large pieces weighing altogether 2.26 kilo., and 127 small fragments weighing together 2.865 kilo. A cast-iron shell of 15 cm. and 27 kilo. produced 376 pieces of more than ten grams, and 828 pieces from one to ten grams. It was noticed that fragments weighing less than one gram traversed boards 25 mm. thick.

A projectile of 15 cm. and six cal., containing 9.935 kilo. of gun-cotton, buried vertically in the earth, the bottom being 25 cm. below the soil, produced a crater four meters in diameter and 1.3 meters deep, and having a crater of 7 m^3. capacity. An eight kilo. petard gave a crater of 3.5 m. diameter, 1.5 m. deep and 6 m^3. capacity; with a charge of sixteen kilo. they obtained a diameter of 5.1 m., depth 1.56 m., capacity 12 m^3.

In November, 1885, the *Revista di Artigleria e Genio* announced that the German Government had adopted the Walsrode granulated gun-cotton for charging shells.

Experiments were made at this station during the past and present years in testing the safety of our service gun-cotton for use as shell charges in service guns when the shell were not fused. The only guns we had at hand were the Dahlgren 24-Pdr. howitzers and the 20-Pdr. M. L. R., and, as it was deemed advisable and, in fact, essential to use the gun-cotton in its compressed condition, special elongated projectiles had to be made for these guns.

The shell for the 24-Pdr. were made of cast iron. They

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had an exterior diameter of 5¾ inches, interior 5 inches, interior length 8 inches. They were fitted with a base plug and had a curved head. The shell were all fired with service charges of powder. As the interior diameter of the shell was much larger than the diameter of the gun-cotton discs, dry sawdust was rammed in to fill up the space.

In the first four rounds from this gun the shell charge consisted of three and one-half discs of wet gun-cotton, weighing 4½ pounds for each, while the loaded shell weighed from 30 to 32 pounds. In the first round the gun was fired point blank at the masonry escarpment of the fort on Rose Island 50 yards distant from the muzzle. There was no explosion, and the shell broke up on striking, scattering the gun-cotton, but without setting fire to it.

In the second round the shell struck in the crevices of the masonry and buried itself in the earth behind. It was recovered and found to be perfectly intact, except that a fragment was broken off the projecting base plug.

In the third round the shell was fired up the Bay. It was a straight-line shot, and the shell richocheted on striking the water, but it neither exploded or broke up.

In the fourth round the shell recovered from round two by digging from butt was fired again at butt. The shell broke up on striking, but there was no explosion and, on digging into the butt, the point of the shell, with a disc of gun-cotton and sawdust firmly imbedded in it, was recovered.

In the fifth round the charge consisted of one dry and three wet discs; in the sixth round, of two dry and two wet; in the seventh, eighth, ninth and tenth rounds, of four dry discs each. In all these cases the shell were fired into the escarpment, and in no case was there an explosion, either in the gun, during flight or on impact,

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though the projectiles broke up on impact. At the time of breaking up, a little of the dry gun-cotton was sometimes set on fire, but most of it was scattered about and recovered. Occasionally, whole discs were recovered, but they were much compressed, distorted and cracked, showing how severe the blow was to which they had been subjected.

The shell used with the 20-Pdr. were made of 4-inch steel tubing ¼ inch thick, with solid conical heads and movable base plugs, and were of such a diameter as to just take the gun-cotton discs, so that no packing was used, only an asbestus gasket being placed over the base plug. The service charge of powder (2 pounds, rifle) was used and all other service conditions preserved in these experiments.

In the first four rounds the shell were loaded with from 4 pounds, 9 ounces to 6 pounds, 6 ounces of service wet gun-cotton, and they were fired into the butt. There was no explosion in any case, the shell were broken at the butt and some of the gun-cotton scattered about, but the bodies of the shell were recovered, distorted and crushed, but still tightly filled with gun-cotton.

In the next six rounds the same gun and similar shell were used, but the charges were all of dry gun-cotton, and instead of being in one compact mass, as in all the previous experiments, they were composed of split ½-inch discs, so there was some play to the charge.

In the first round the same results were obtained as with the wet gun-cotton. In each of the remaining five rounds the shell broke up in the gun, but there was no explosion and no damage done.

These experiments were continued at the Naval Ordnance Proving Ground, where six rounds were fired from the 6-inch B. L. R., known as the South Boston gun. The

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projectiles used were elongated shrapnel cases with removable heads. They weighed, after their contents had been removed, from 75½ to 77 pounds, and they held from 6 to 6½ service g. c. discs, *i. e.*, from 4 pounds, 8 ounces to 4 pounds, 14 ounces of dry gun-cotton, but, as the shrapnel had a larger diameter than the gun-cotton, and, as the cavity was also much contracted at the base, there was a large space which had to be filled with sawdust. The walls of the projectile were $1\frac{1}{2}$ inch thick at the mouth and increased in thickness as the space was contracted.

Wet service discs were used in the first five rounds. The weights of the loaded shell varied from 81.5 to 83 pounds; the weights of powder charge from 25 pounds of Dupont Brown Prismatic to 29 pounds of Sphero-Hexagonal, and the registered chamber pressures from 8.45 tons to 13.8 tons. The shell were fired down the Bay, and in no case was there an explosion or breaking up of a shell.

In the sixth round the shell charge consisted of one dry service disc, the rest of the space being filled with dry sawdust packed as closely as a man could ram it with a short wooden rammer. The weight of the loaded shell was 78 pounds, of powder charge 28 pounds S. H., and the chamber pressure, as registered, was 13.1 tons. On firing, the shell was blown out of the gun in small fragments, but there was apparently no explosion of gun-cotton as the pressure registered was normal, and the gun was not affected beyond an almost imperceptible scoring at the muzzle. Evidently, in this case, the sawdust was not compact enough to support the walls of the shell.

Dynamite was invented in 1866 or 1867, yet certain persons have recently* asserted that in the years 1862,

Proc. Nav. Inst. 14, *152;* 1888.

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'63 and '65 they repeatedly fired James, Hotchkiss, Rodman and Parrott shell loaded with chemically compressed dynamite. However, this may have been, we find that in Sweden,* in September, 1867, seventeen shell, each charged with 1.65 pounds of dynamite, were fired from an 18-pdr. howitzer loaded with about two pounds of gunpowder. No premature explosion occurred. In Norway* in the winter of 1870–71, some trials were made with a 6.8-inch Krupp gun. At first the shell was packed full of dynamite. Several preliminary shots were successful, but when the charge was increased to 1.65 pounds of gunpowder the shell burst in the bore. Continuing the same trials, shell filled with water, and primed with an ounce of dynamite in a copper extension of the fuse plug, were fired with full charges without accident. During the siege operations of the 2d Corps of the Army of Versailles,† in May, 1871, two shell charged with dynamite were fired without accident into the hostile lines; one was from a 24-pdr. howitzer and the other from a mortar. The dynamite was enclosed in a rubber bag held in position with gunpowder, and was ignited by a time-fuse in both instances.

In May and June, 1874, Comdr. A. S. Barker,‡ U. S. N., fired nine shell filled with dynamite from a 24-pound howitzer, at the Torpedo Station. He used service charges of gunpowder, and used his shell under service conditions, yet there were no cases of premature explosions, either in the bore or after leaving the piece. Three of these shell, unfused, were fired into the wall of an old bomb-proof at a distance of 13 feet, and they exploded on impact. The remainder were fitted with Bormann time fuses and fired up the Bay. None of the shell burst

*Memorial de l'Officier du Genie 20, 243-244.

†Loc. cit p. 246.

‡Proc. Nav. Inst. 12, 547-561; 1886.

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prematurely, and part of them burst successfully at the time fixed.

Comdr. Barker was so much encouraged by the results obtained that he recommended and urged, then and afterwards, that he be permitted to extend these trials to our largest calibre smooth bores.

In 1883 the Ordnance Board, U. S. A., fired five shell, each charged with 6½ ounces of explosive gelatine, and fitted with Schenkle's percussion fuses, from the 3-inch wrought iron rifle. All the shell burst after leaving the gun and before reaching the target. The explosive had been on hand for some time.

In 1884 Comdr. Folger, U. S. N., fired 22 rounds in 12-Pdr. shell, the last ten being under service conditions. Each of these shell contained 5½ ounces of dynamite and a little oakum to serve as a packing. There was no premature explosion, though one of the shell exploded on impact with the water. Five of the shell carried ordinary time fuses, and these exploded at the point and time intended.

The same year the Ordnance Board, U. S. A., fired two rounds with a new lot of explosive gelatine from Nobel's Explosive Co. at Glasgow, the same gun and projectiles being used as above. The first shell broke up on leaving the gun, the second broke up on impact with the target, but as it struck sidewise it evidently did not take the groove. As this last was the only shell in seven which did not break up prematurely, it was thought that the others had been broken up owing to the heat generated by friction between the rotating projectile and the explosive, so three projectiles were prepared for the 3.2-inch gun with hollow wooden cases closed at the bottom and lubricated on the exterior. They contained one pound each of the explosive. The first shell did not explode until reaching

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the target. The second burst soon after leaving the gun, but its wooden case had been cracked in filling. The third burst in the gun and destroyed it. The projectile was an old one, and it was thought the shell might have been ruptured by the powder charge, or that the base plug fitted imperfectly. So new projectiles were prepared for the 8-inch M. L. R. They were made of cast iron with an ogival head connected to the body with a screw thread. To avoid friction between the explosive and the walls of the rotating shell, the explosive was packed in a paste-board cylinder divided longitudinally into four compartments by two pieces of wood. The cylinder fitted the shell loosely and was coated on the outside with plumbago and tallow. The shell contained 5 pounds, $3\frac{3}{16}$ ounces of explosive gelatine. The powder charge was 40 pounds Dupont S. H. powder. A hollow rubber buffer 6 inches long and 1 inch thick was interposed between the powder charge and shell. The shell struck the target and burst on impact. A second shell, without the wooden diaphragm, but otherwise like the first, broke up on leaving the gun. A third shell, arranged just as the first, broke up on impact. It being considered that these trials showed the case to be superfluous, and that a stout diaphragm which would cause the explosive to rotate with the shell would prove sufficient, one was prepared with a copper diaphragm let into grooves in the sides of the cavity. The shell contained 8 pounds, 13 ounces of explosive, the powder charge being as before, and it broke up on impact. As, from the construction, these shell were not very strong, steel shell with solid heads and heavy screw base plugs were made. One of these, containing a copper diaphragm and 5 pounds of explosive gelatine, was fired with 40 pounds F. V. M. hexagonal powder and destroyed the gun. The gelatine had been on hand a year and was

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uncamphorated. A second containing a new supply of camphorated gelatine was fired from the 8-inch M. L. R., and it burst in the muzzle of the gun.

It should be noted that in the course of these experiments three Butler shell charged with gunpowder and containing fulminate fuses broke up just as those containing explosive gelatine did.

In 1886 another round was fired with a projectile devised by Mr. D. P. Hill from a Butler shell, by boring through the base so as to introduce a brass cylinder carrying the charge (5 pounds) of explosive gelatine. The case was fixed to rotate with the shell and carried an elastic cushion at the front and rear within the shell, while there was a buffer of six inches of felt behind and attached to the shell. The shell was fired from the injured 8-inch M. L. R. with 40 pounds of Dupont E. V. powder, and it shattered the gun to fragments about the seat of the projectile.

In 1884 tests were made with a special form of shell, to be loaded with dynamite or explosive gelatine, which was designed by Mr. F. H. Snyder. It consisted practically of a sabot, built up of gelatinized fibre, leather and copper discs, to be placed next the powder charge, next to this a brass case holding a cellular rubber buffer, next a wooden plunger for compressing the buffer and then a shell-like magazine for holding the explosive.

On July 25 two rounds were fired with 3-pound charges of powder from a 6-inch gun there being 8 pounds, 8½ ounces of dynamite in the shell. The first shell struck about 200 yards from the gun and broke up without exploding. The second exploded in the bore and destroyed the gun.

In October five rounds were fired with thicker-walled shell. The powder charge was as before 3 pounds, and

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the shell charge from 7 pounds to 8 pounds, 8 ounces of dynamite. None of these shell exploded prematurely, but some failed to explode on striking. As the projectile weighed 60 pounds, the powder charge was much too small to obtain any suitable range, and it was determined to increase it to 8 pounds. A preliminary round with a shell loaded with sand having shown that the projectile was strong enough to resist rupture, a loaded shell containing 6 pounds, 12 ounces of dynamite was fired which destroyed the gun.

In 1885 Snyder used a 12-pdr. cannon, and with a charge of $1\frac{1}{3}$ pounds of powder he claims to have successfully fired projectiles containing five pounds of dynamite. Five rounds were fired in Washington in March, 1886, from a 6-inch B. L. R. with shell containing from eleven to twelve pounds of forcite. There were no premature explosions, and the shell exploded on impact doing considerable execution on the rock target. In 1888 this system was tried by the Turkish Government at Agha Deressi, a 6-inch B. L. R. being used and the shell being charged with 10 pounds of explosive gelatine. The target, which was 656 feet from gun, consisted of a 12-inch laminated steel plate backed with 12 × 14 inch oak beams, the whole weighing twenty tons. A single shot overthrew the target, which fell on its face, while ten rounds were fired without accident of any kind and without injury to the gun.

In 1886 Lieut. J. W. Graydon fired 52 rounds from the $4\frac{1}{2}$-inch siege gun with unfused shell containing dynamite No. 1. The target was a rocky cliff at a distance of 2200 yards. None of the shell burst prematurely, and all but two were observed to burst with a loud report on impact. It was not stated how much dynamite was used; the method of loading the shell was by first lining it with

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asbestus paper—two thicknesses on bottom—and then inserting packets of the dynamite wrapped in paraffined paper, and ramming them with wooden rammers until the shell was filled. When loading the gun, eight asbestus wads were placed between the powder and projectile. The inventor claims that it takes a given amount of heat to explode the dynamite, and he gets a certain amount from the gunpowder, more by friction in transit and enough more on impact to explode the shell.

This system was tested by the Ordnance Board at Sandy Hook in December, 1887, the 7-inch Ames M. L. R. and steel shell weighing 122 pounds, containing 2.3 pounds of dynamite No. 2, with a powder charge of 23 pounds being used. The shell were fitted with base plugs for convenience in loading, and a fuse was provided. The target, which was 110 yards from the firing-point, was a section of a wrought-iron monitor turret 14 inches in thickness and made up of two 7-inch plates, each of which was divided horizontally into two sections so disposed as to break joints, the joint in the front plate being one-third the distance up from the base. The whole was roofed with an iron plate, 3 inches thick, and weighing from 12 to 15 tons, which projected 1 foot beyond the face of the turret and was secured to the latter by several $1\frac{3}{4}$-inch wrought-iron bolts. The target had no backing and was not braced or supported. It had been used as a great-gun target before, and shot-marks were visible on its surface, while there were several noticeable cracks in it. The first shell which struck the target was a glancing shot, and not a "point on" shot, as was desired to test the penetration. It made an indentation, nevertheless, three inches deep and, though unfused, it exploded with great violence. As a result, the roof of the turret was lifted off and blown twenty-five feet to the

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rear, breaking seven bolts, each one and three-fourths inches in diameter, used to bolt the front and rear plates together. It also made a crack ten inches long in the front plate and about eighteen inches long in the rear plate. The wreckage was very marked. The two seven-inch plates of the turret proper were also torn apart a distance of five inches, breaking off the bolt heads which secured the plates together.

The second shot struck in a mark one inch deep that had been made by an empty cast-iron shell, deepening the impression to three and one-eighth inches, sixteen inches below the first shot. It continued the crack made by the first shot upward to the top bolt holes and downward to the horizontal joint, the length of this crack being five feet two inches. This was also a glancing shot, the same as the first. The wreckage produced by this shot was even greater than that of the first, the two seven-inch plates forming the turret proper, which were torn apart by the first shot, being still further torn apart to the extent of seven inches. Numerous bolts were also broken and displaced, and the rear plate cracked from the embrasure to the bottom of the turret.

The third shot struck in an old indentation three inches deep and penetrated the first plate seven inches and the second plate one inch. The front plate was broken, a piece two feet eleven inches by three feet three inches being thrown eighteen feet to the left of the target. The cracks in the rear plate were opened, five new cracks made about nine inches long, and the plate opposite the point struck bulged out to the rear three inches. The shot completely destroyed the left side of the target, the penetration of the front plate being effected before the explosion of the dynamite, and its wrecking energies being entirely exerted on the turret. The weight of the

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piece blown out was variously estimated at from one and a half to two tons. The two main seven-inch plates composing the turret were also still further separated and numbers of bolts blown off.

Four other shells were fired at different ranges, one reaching the full range of the cannon, estimated at four and a half miles, out to sea.

In 1887 the N. Y. Dynamite Projectile and Gun Co. presented a projectile for the 3.2-inch rifle consisting of a shell with a piston rod attached to its base and on the end of this an air cylinder, all being of steel. The air cylinder was designed to take up the shock of discharge by the gradual compression of the air within it. Two sets of experiments were made, blasting gelatine being used as the shell charge, and in both cases the gun was destroyed.

A somewhat similar projectile, in which the same principle was involved, was presented by Mr. W. M. Brisben, but was not submitted to trial as it was found to be faulty in design and impracticable.

According to current report, experiments in firing shell loaded with dynamite, after a method devised by Mr. B. D. Stevens, were tried October 11, 1887, at the State Arsenal, Montpelier, Vt. The piece was a 12-pound brass Napoleon; the shell charge one-half pound of 35 percent dynamite, a time fuse being used and the usual service charge of two and a half pounds of powder. Five rounds were fired without any premature explosion. We have no information as to the device employed further than that the shell was double.

In 1885 the Ordnance Board tested a device of C. P. Winslow's, which consisted of a shell containing two glass jars, one within the other, the inner one containing a mixture of nitric and sulphuric acids in the proportions by volume of 4 : 3, and the outer one glycerine and sul-

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phuric acid in the proportions of 6 : 1; the volumes of the liquid mixtures being the same in each jar.

The projectile was formed, like a Butler shell, with an appendage resembling a cascabel, the neck of the appendage, to which a wrench was fitted, being hexagonal. The part corresponding to the knob was a cylinder terminating in a spherical segment. The projectile was divided into two sections, the interior part being a cylinder with an ogival head, and containing a cavity in which the ingredients to produce an explosive compound were placed, and terminating at the rear end in a screwed tenon, by means of which it was fastened to the rear section. The rear section was provided with a cavity intended to receive a cast-iron plunger and a charge of rifle powder. Near the base of the projectile was a circumferential groove in which time-fuse composition was driven, and this groove was connected with the rifle powder in the rear of the plunger. An axial chamber was bored in the plunger and contained a small charge of rifle powder, the rear of this chamber being closed by a screw-plug, containing a vent filled with slow-burning composition.

The jars were fastened together by screw-caps, and were placed within a tin cylinder, open at both ends, which fitted the shell cavity. Stout cross-bars traversed the open end of the cylinder, and the exterior glass vessel was fastened to the bars by strong bands, which, aided by rubber straps, were designed to prevent the rupture of the jar when the piece was fired. The rupture was intended to be effected in the following manner: The time-fuse was cut at any desired point, and when the projectile had traversed a certain portion of its trajectory, the charge of rifle powder in the rear of the plunger was to be fired and the plunger to be forced violently forward, thus

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breaking the bottles, and, in connection with the rotation of the shell and the broken fragments, causing an intimate mixture of the glycerine and the acids, and forming the explosive compound. When the projectile struck a resisting object, the shock of impact was expected to cause the explosion of the compound thus formed, or, if this did not occur, then the charge contained in the axial chamber of the plunger was relied on to bring about the explosion.

Three rounds were fired from the 8-inch M. L. R. In the first 35 pounds of powder were used, and it was thought that the projectile was broken by the shock of discharge. In the second 30 pounds of powder were used, and the fuse was set for five seconds. The shell burst in the air in two and one-half seconds, and from the peculiar appearance of the smoke the rupture was regarded as due to the explosion of a substitution (?) compound. In the third round, fired with a 30-pound charge, over water, no explosion took place. The fourth projectile was exploded by means of an electric primer in an inclosure. The shell broke at the screw-thread into two pieces, the head being thrown some 25 feet out of the inclosure. The bottom was forced against the side of the inclosure.

In conclusion the Board reported that the acids can be safely transported to any point, the mixture can be effected without danger, and a shell arranged to contain them may be fired from a gun without injury to it. With the mixture used an explosive compound is probably formed, although the proportions of the ingredients used were not such as to give the best results. If they had been, and if the greatest possible amount of nitroglycerine producible by the ingredients which the shell cavity could contain were formed, it is not thought that

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the effect would be equal to that resulting with an ordinary bursting charge of gunpowder. The Board therefore recommended that no further trials be carried on with devices closely resembling it in principle.

In October, 1887, experiments were made at the Torpedo Station in firing nitro-glycerine from 24-Pdr. howitzers according to a method proposed by Mr. Serge D. Smolianinoff. He treated nitro-glycerine so as to render it insensitive, poured the liquid into the shell, completely filling it, and then fitted in the fuse hole a burster with time fuse attached. The liquid, as used here, contained 97 percent of nitro-glycerine, and the service shell held from 1 to 1.5 pounds of the liquid. Twenty rounds were fired with service charges of gunpowder. Five of the shell were unfused, and were fired into the masonry escarpment, 50 yards from gun. All broke up without any perceptible explosion. The remainder were fused and fired up the Bay, and, with the exception of three, they exploded in mid air, at the time fixed, with a sharp report and scattered the fragments over a very wide area.

The Board reported: "The experiments lead us to the conclusion that the method of firing nitro-glycerine from powder guns, which Mr. Smolianinoff has submitted to us, is a perfectly feasible one for the conditions such as have been obtained in our experiments, and we would strongly recommend that the experiments be extended so as to test its value for guns of greater caliber, with larger charges of powder, and capable of throwing projectiles containing relatively much larger amounts of nitro-glycerine."

Previous to the Newport experiments Mr. Smolianinoff claimed to have fired over 300 shell from a condemned 20-Pdr. rifled Parrott, using an 8-inch conical shell completely filled with the prepared nitro-glycerine, and a

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3-pound charge of Dupont F. F. powder, and that he had not a single premature explosion.

In November, 1887, three rounds were fired at Sandy Hook by this method from the 100-Pdr. Parrott with shell weighing from 82 to 89 pounds and containing 4.1 to 4.6 pounds of the prepared nitro-glycerine; 18 pounds of Dupont powder were used giving 1404 f. s. velocity and 26700 pounds pressure. The target was in every respect similar to that used in the Graydon experiment.

In one round no fuse was used, in the other two the shell were fused. All exploded on impact but did no material damage to the target. As the cast-iron shell used were very weak and adapted for a nose fuse, penetration was impossible, and hence no really useful result could be looked for beyond the proof of the safety of the method.

The Gruson system of employing high explosives, which was patented in Germany in 1879, embodies the safety principle, first set forth by Dr. Sprengel in 1873, of using two or more substances which are harmless by themselves, but which form a very powerful explosive when mixed, and keeping them apart until wanted for use. This is accomplished either by placing the substances in the shell in fragile vessels of glass, porcelain, or similar material, which are strong enough to resist the jolts and jars incident to transportation and handling, but which are not strong enough to resist the shock of discharge in the gun, or it is done by dividing the shell into a number of compartments by means of suitable diaphragms. When the first method is used the fragile vessels must be enclosed in rubber, felt or other elastic substances to prevent accidental fracture. These shell have been constructed with base fuses, and without fuses, the latter being armor-piercing shell designed to be exploded by impact.

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Various explosives may be used in these shell, but Gruson adopted hellhofite. In the earlier experiments the nitric acid was contained in the head of the projectile and the nitro-benzene in the base. When explosion after penetration was required the materials were placed in the reverse order, and a delay-action fuse in the base retarded the operation of the mixture until the greatest point of penetration had been attained.

In a trial in 1883* of 15-cm. shell, six of them, containing 1.1 kg. of hellhofite, were fired against a parapet, and they effected about four times the damage which six shell, containing gunpowder, under the same conditions did.

Twelve Gruson 15-cm. shell, containing 1.9 kg. of hellhofite, were fired at Palmanova in 1884 with a charge of 1.2 kg. of powder, and four with a charge of 1.4 kg. of powder. Three 24-cm. shell containing 5.53 kg. were also fired with a powder charge of 4.3 kilos. There were no premature explosions, but the projectiles were found wanting in accuracy and to be inferior in effect to similar projectiles charged with gun-cotton, though superior to gunpowder.

Experiments with these shells are also said to have taken place in Denmark, Sweden, Switzerland and England, but no data of the trials is at hand, though the results in the first country are said to have been very favorable to the new explosive, while in the last they were not very satisfactory.

There are probably no experiments of late which have excited more interest or aroused greater curiosity than those currently reported as having been made in France in firing shell filled with *melinite* from powder guns, and this is largely due to the mystery in which the whole subject, owing to a wise policy on the part of the French

*Ill. Nav. and Mil. Mag., 5, 402-412; 1886.

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government, is enveloped. What seems certain is that the explosive has been thrown in this way repeatedly in large charges and that the success attending its use has led the French to adopt it as a service explosive and to store in their magazines a large supply of projectiles filled with it, for use in war. There is little doubt that experiments in firing it have been carried on with the *Belliqueuse* as a target and though it is said that no effect was produced by this fire on the armored portion of the ship, the shell which struck the unprotected parts created "terrible havoc," and that as a consequence, the French Naval experts advocate a reversion to complete armor and the designs of several ships now building, such as the *Brennus* and the *Dupuy de Lorne* have been modified to meet the fire of high explosive projectiles. Experiments recently made in England with *melinite* and gun-cotton shell, in which the *Resistance* was employed as a target, are also reported to have given results similar to those yielded by the *Belliqueuse* experiments, but here again a secretive policy is pursued.

We have stated in Lecture V. that *melinite* is said to be picric acid in a particular fused and consolidated condition. In a recent work* Max Dumas-Guilin says it is a mixture of picric acid and a collodion, while elsewhere I find it given as being a mixture of fused picric acid, in granules, with tri-nitro-cellulose dissolved in acetic ether. Dumas-Guilin refers us to the German journals for an exact description of its composition. He states that shell containing 33 kg. have been fired at Bourges; that this corresponds in power to 100 kgs. of powder; and that the *melinite* shell have produced destructive effects equal to those obtained by the Germans with gun-cotton shell. The Office of Naval Intelligence reports† that the French are said to

La dynamite de guerre, Paris, 1887.

†*Gen, Information Series*, 7, 373; 1888.

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have succeeded in firing *melinite* shell from high-power guns with velocities as high as 2000 f. s. The weight of *melinite* in this case is not mentioned, but it is known that charges of nearly 70 pounds have been repeatedly fired from the 22-cm. mortar with velocities of over 1300 f. s.

Trials have been made with romite in Sweden, but nothing is known further than that small shell charges were fired from an old 10-cm. M. L. gun with an initial velocity of 400 m., and that there were no explosions until impact.

Although many devices, such as catapults and arrows tipped with high explosives, and balloons arranged to automatically drop explosives, have been suggested, the best perfected device for projecting high explosives, in use in this country, is that known as the Pneumatic Torpedo Gun, and although, according to Capt. Zalinski, U. S. A., "in no way is this weapon to be compared with powder guns, nor in any way to replace them," it seems proper to speak of the weapon in this connection.

The application of the expansive force of steam or of compressed gases to the throwing of projectiles is no novelty, as it was shown long since in the Perkins' steam-gun and the common air gun that it could be availed of for this purpose, though these weapons could not compete in efficiency with the gunpowder gun. The application, however, of this force to the throwing of projectiles charged with high explosives is novel, and is due to Mr. D. M. Mefford of Ohio who in 1883 designed and constructed a 2-inch gun which was submitted to the War Department, and consigned by the Department to Lt. E. L. Zalinski, 4 Art., U. S. A. for trial. From that time the latter has devoted himself most assiduously to developing the full power of this weapon and he has devised a most

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ingenious and valuable fuse, for use with it, which seems equally applicable to projectiles thrown from gunpowder guns.

The following description of this weapon is taken from Capt. Zalinski's address before the Naval Institute.*

The gun barrel consists of a very light tube having, at present, a smooth bore. As the firing pressure used does not exceed 1000 pounds per square inch, it will be seen that, if made of steel or aluminum bronze, it need not be more than one half inch thick even in calibers as great as twenty inches; a greater thickness has been used in the 8-inch and 15-inch guns, for the purpose of obtaining somewhat greater rigidity and to lessen the chances of mechanical injury in transportation and manipulation. Where it is important to eliminate weight, as on ship-board or on torpedo boats, these tubes can be made very light indeed, especially in cases where they are placed at a fixed angle. When the machine is to be movable for elevation or direction or both, the barrel is supported on a suitable truss.

The breech mechanism is ordinarily a simple gate arranged so that the valve mechanism cannot function until the breech is closed and latched. The valve is known as a balanced valve, so arranged as to open and close by a single movement of the operator. The time of opening and closing can be varied by an adjusting device so that any desired loss of pressure will ensue. In this way the range can be changed without change either of elevation or pressure. In addition to this means of controlling the range, there is a device for throttling the passage-way between the valve and the reservoir of the gun, so that although the valve may open and close in a uniform time, the amount of air which can pass into the gun in that time

*Proc Nav. Inst. 14; 1888.

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can be varied. A more complete and accurate control of the range can be obtained in this way than in any other. The size of the passage-way can be quickly regulated to a hair's breadth. In the case of a vessel advancing or retreating from a target, the opening can be constantly changed to conform, to the variations of range, much more quickly and accurately than can be accomplished by corresponding changes of elevation of a gun.

The air reservoirs used thus far consist of wrought iron lap-welded tubes of 12¾ inches and 16 inches outside diameter and from ½ to ⅝ inch thick. These tubes are from 18 to 20 feet in length. The reservoir tubes from which the air for firing is directly drawn are known as the "firing reservoirs." This reservoir will, as a rule, have five times the capacity of the bore of the gun. Experiments are under way with a view of producing very light reservoirs, both by wire-winding and by cold drawing of brass and steel. It may be well to mention here that the pressure in the reservoir may be reduced by a single firing to any predetermined amount, the valve being adjustable to accomplish this automatically. The most economical results are obtained with the air acting expansively. A loss of 10 per cent to 12 per cent with a reservoir of five capacities of the gun bore is the maximum which can be used with any appreciable advantage. Where it is desired to fire a large number of rounds with great rapidity, an auxiliary storage reservoir is used, into which the air is compressed ordinarily to twice the pressure to be used in the gun. After each discharge the air is drawn from these, to restore the pressure in the firing reservoir to any desired point.

The air compressors may be of any type capable of giving the high pressure to be used. The compressors of the Norwalk Iron Company have been used thus far.

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These compressors perform the compression in two stages, there being an intermediate cooling in passing from the first compression to the last. Where cooling processes are to be used for other purposes on shipboard, the air compressors can be utilized. They may also be of use where the pneumatic gun carriage system is introduced.

The shell is made at present of brass tubing and castings, made as light as consistent with the necessary strength for handling and in being fired. The shell is retained in its proper trajectory by means of the tail tube, to which spiral vanes are attached. It is centered in its passage through the bore and kept from metallic contact with the same by means of non-metallic pins in the head, the leather gas check at the rear end of the cylindrical part of the body, and by the vulcanized fibre projections riveted to the spiral vanes of the tail.

They have recently succeeded in making the conical point and cylindrical portion of the shell of a single seamless piece, it being produced by hydraulic pressure. This was not considered easy of accomplishment in view of the fact that, for the 15-inch shell, the piece is $14\frac{3}{4}$ inches outside diameter, 80 inches in length, and $\frac{1}{8}$ inch thick. The conical point is made strong enough to resist crushing from impact with water, but so thin as to readily crush when striking a solid target.

The charge thus far has been uncamphorated explosive gelatine, having a core of dynamite. This core is for the purpose of producing a complete detonation of the less sensitive explosive gelatine. Zalinski prefers compressed dry gun-cotton for this purpose, as cold weather does not affect its properties as a detonating substance. At the front and rear of the charge he would use camphorated gelatine to diminish the chances of explosion by shock, both in starting the shell and in striking the

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target. For this purpose also, a diaphragm is placed so as to stop off the charge some distance from the point; this gives time for the detonation of the charge from the *rear end* before the front can be exploded by shock. To guard still farther against the possibility of explosion by impact and give time for the electrical primer to act, it may be necessary to place a cushion of felt or other elastic substance in front of the diaphragm. This can only be determined by actual experiment against armor plates.

The earliest experiments with the pneumatic gun demonstrated that the ordinary fuse arrangements were insufficent to obtain the best results with high explosives. It was found necessary to produce the initial explosion at the *rear* end of the charge, in order to produce the maximum effect on a solid target, and it was important, therefore, that this explosion should take place an instant *before* full impact.

To obtain the very important torpedo effect which is the primary object of the pneumatic torpedo shell, it is necessary to cause the explosion to take place an interval of time *after* striking the water. The tamping, due to the submersion, is thought sufficient to develop the maximum energy of the charge, and this acts against the more vulnerable under-water hull. Where countermining is to be attempted against ground mines, it is desirable to ensure some of the shells getting to or near the bottom before exploding. Above all, the fuse must be assuredly safe in storage and in handling. Consideration of these requirements led to the development of the electrical fuse.

This consists of four parts:

1. The electrical battery; 2. The low tension primer; 3. The circuit breaker; and 4. The detonating cap.

The chloride of silver battery has been selected as being most suitable. Although the electro-motive force is low,

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the internal resistance of the battery, as made, is very low, and a small single element suffices to bring the bridge to a red heat. But to ensure against accidental increase of resistance in the circuits and to reduce the *time* required to fire the primer, one set of batteries is made quadruple, while the other two sets are double. Each set is arranged in series. All of the elements of the quadruple battery, which is in the rear end of the shell, are wet with salt water before insertion into the shell. One pole of this battery is connected, through the primer embeded in the fulminate of mercury detonator, to the metallic body of the shell; the other pole is connected with a light copper cone fixed in the conical point of the shell and insulated therefrom. The shell striking any solid target, either normally or otherwise, will cause the outer shell to crush in on the insulated cone, close the wet battery circuit and explode the charge.

A double dry battery is placed in the point and another at the rear end. This last is inserted as a matter of precaution rather than as an absolute necessity. One element of each of these double dry batteries is wet up, and is ready for action as soon as the salt water enters the other element. Upon the shell entering the water, the dry element becomes wet, and the current then passes through a primer which ignites a time train. This in turn ignites the detonator. The time train is adjustable so that a variable submersion before explosion can be obtained. The rear dry battery acts in the same manner should the other fail. If it is desired to cause the shell to reach the bottom before exploding, a water cap is attached to the dry battery in the point of the shell. Provisions are made to protect the front and rear batteries from moisture until the shell has left the bore of the gun. If fighting in fresh water, a small bag of salt is placed in the dry battery fuse case.

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The circuit breaking device ensures all circuits being retained open until the shell has left the bore of the gun. If anything should be amiss with the circuits, no explosion will result until the shell is some distance beyond the muzzle. Nothing can be amiss, however, if proper care is taken in making up the shell, arranging the circuits, and testing. The circuits can be tested at any time before inserting either the batteries, primers, or detonators; there need be no guess work as to the condition of the circuits at any time. The batteries, primers, and detonators need not be inserted until just before using. A double set of circuit breakers, primers, and detonators are used to increase certainty of action. To guard against the chances of breaking the very fine filament of platinum wire constituting the wire bridge, it is embeded in a very solid cake of compressed gunpowder.

During the past year this gun has been subjected to two notable trials in the presence of the Naval Pneumatic Dynamite Gun Board.* The first, which was for destructive effect, took place Sept. 20, 1887, in N. Y. Harbor, the the gun being the 8-inch one which was mounted at Fort Lafayette and the target being the condemned schooner *Silliman*. She was moored head and stern, the stern being toward the firing-point and 1864 yards distant from it. Her dimensions were; length, 79 feet; breadth, 22 feet; depth, 8 feet 6 inches. She had her two masts and bowsprit standing.

Six rounds were fired. The projectile in the first one was loaded with sand; each of the others contained 50 pounds of explosive gelatine, 5 pounds of dynamite No. 1, and two 30-grain mercury fulminate detonators. The weights of the projectiles varied from 136 to 137 pounds and the times of flight from 10.5 to 10.7 seconds. The weather was fine and there was no wind.

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The first round was a trial for range. Weight of projectile loaded with sand, 141 pounds. Elevation 14° 52′. Aimed to right so as to avoid the target. Firing pressure 590 lbs; final pressure 490 lbs. Struck 24 yards to the right and 27 yards short, reckoning from the stern of the schooner.

The second shot was aimed to hit the target. Elevation 14° 52′. Firing pressure 595 lbs., final pressure 485 lbs. Struck 8 yards to left and 10 yards short, entering water properly for torpedo action, but did not explode. No satisfactory reason for this failure was discovered.

The third shot was aimed to hit the target. Elevation 14° 56′. Firing pressure 605 lbs., final pressure 200 lbs., (due to accidentally opening the valve a second time). The shell struck a little astern of and on starboard quarter of the target, entering the water at once and exploding, apparently, as estimated by the character and height of water thrown up, at the proper depth for torpedo action. On boarding the schooner it was found that the mainmast had been broken off just above the deck and had fallen to port. The mast, where it broke off, was very rotten, (there being only a slight shell of sound wood on the outside) while besides it had been only slightly supported. Bulkheads were thrown down, and there were other evidences of the shattering effect of the explosion. There was about two feet of water in the schooner, and the planking under the starboard quarter appeared to be breached. The moorings on the starboard quarter were disturbed so that the vessel drifted a few feet from the gun and took a position slightly across the line of fire, the stem being to the left as viewed from the gun.

The fourth shot was aimed to hit the target. Elevation 14° 56′. Firing pressure 610 lbs, final pressure 505 lbs.

*Gen. Inf. Series 7, 348-351; 1888, Office of Naval Intelligence.

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The projectile struck the water a short distance from, and abreast of the starboard quarter, and entering the water, it exploded about abreast of the centre of the schooner and very near if not under her. The torpedo action of the projectile was perfect, and it follows that the under-water fuse acted at the proper depth for this target, i. e.: from 6 to 10 feet. The centre of the schooner was raised well up, her back broken and penetrated by a column of water, and the vessel fell back a complete, disintegrated wreck. Examination of the wreckage showed that the centre of explosion was near enough to produce that peculiar bruising and twisting effect upon the sound wood which is characteristic of detonating high explosives. The wreckage, for the most part, was still held together by the chains and moorings though it drifted about 25 feet to the left and away from the gun.

The fifth shot was aimed at the foremast of the wreck. Elevation 14° 52′. Firing pressure 620 lbs., final pressure 520 lbs. The projectile exploded 3 or 4 feet above water over the wreck and abaft the foremast, owing, it is supposed, to its having struck some of the wreckage which caused the above-water fuse to act.

The sixth shot was aimed at the wreck of the foremast. Elevation 14° 52′. Firing pressure 612 lbs., final pressure 520 lbs. Struck abreast of the wreckage, but about 10 yards to the right, and entering the water, it exploded, probably at a depth of 6 or 7 feet, throwing up a column of water, of small diameter, to a hight of at least 100 feet.

The Board say:— "It is very important to observe that in these experiments, undertaken by the company for destructive purposes, the air pressure was reduced from 1000 pounds, the normal amount used in other experiments witnessed by the Board, to about 600 pounds, the elevation being increased by a corresponding amount.

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This could have been done but for one purpose, viz.: to prevent ricochet and insure a proper entry into the water for torpedo action. This indicates the necessity for a high trajectory for a successful action of the projectile.

"Lieut. Zalinski stated that the angle of the fall of the projectile was 18° or 19°. While the accuracy of the gun is such that this high trajectory, with its accompanying narrow zone, may give satisfactory results when the gun is on a steady platform and the target stationary, it will be a very serious condition when both platform and target are moving."

The second trial, which was for rapidity of fire and accuracy, took place Sept. 30, 1887. The shell were carefully selected and loaded with sand. Seven of them weighed exactly 140 pounds each; two, 140.5 pounds each; and one, 142 pounds. The centre of gravity varied between 16 and $16\frac{3}{16}$ inches from the forward end. The firing pressure was 610 pounds; elevation, 14° 56′; times of flight averaged about 11 seconds. The target, consisting of a single buoy with a boat attached, was placed 1868 yards from the gun. During the firing the wind blew with a force of from 3 to 4 (nautical reckoning) and might be termed broad off the port bow, looking towards the target from the gun.

The ten rounds were fired in 10 minutes 45 seconds. Two of the shell broke up and two ricochetted, either being fatal to the torpedo action of the projectile. The flight was remarkably steady. All of the shot fell to the right of the target, and no attempt was made to correct the error, which was probably caused by the wind. The accuracy of the fire may be summarized as follows:

POINT OF MEAN IMPACT.

Short,	13.0 yards,
Right,	13.3 "

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ERRORS.	EXTREME.	MEAN.
Longitudinal	37.0 yards	13.2 yards,
Lateral	8.7 "	3.6 "

Dimensions of rectangle containing 25 percent of probable hits:

Longitudinal	22.3 yards,
Lateral	6.1 "

A sand-loaded projectile weighing 140 pounds was then fired for extreme range. Elevation 32° 42′. Firing pressure 975 pounds; final pressure 825 pounds. Time of flight 24.5 seconds. Estimated range about 4000 yards.

Two sand loaded projectiles representing 100-pound shell* were now fired. Weights, 203 and 204 pounds. Elevation 15°. Air pressure, 750 pounds; final pressures, 625 and 615 pounds. Time of flight 10 seconds. Allowance was made in firing for the effect of the wind. No boat was out to mark the fall of these shots, so that the point of impact could only be estimated, and they seemed to fall about 100 yards short and a little to the left of target. At the time these projectiles were fired the water was lumpy and the wind blew with a force of 4 to 5 (nautical). Neither of these projectiles was as steady in the air as the 60-pound ones were. Upon striking the water the tails of both projectiles broke off, and the shell proper ricochetted a long distance, the first about 20° to the left, and the second about 10° to the right, with a single, very high ricochet trajectory. It is probable that the lumpy condition of the water had something to do with the several ricochet shots of the day. The 100-pound shell carries the centre of gravity about one foot further to the rear than the 60-pounder, while the steel fins have no greater surface, though placed on a longer tail.

The findings of the Board deduced from careful con-

*The shell are designated by the weight of the firing charge.

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sideration of these and other experiments which were witnessed are:

"1. The dynamite gun is a new instrument of warfare, which has its own peculiar function in time of war. It cannot replace any existing weapon, nor can its place be wholly taken by any other.

"2. The value of compressed air as a means of throwing projectiles from a gun is chiefly due to the ability of the gunner to exactly reproduce a shot, or to accurately increase or decrease the range at will, and to the accuracy of fire with low velocities.

"3. The machinery employed by the Company to control air at a great pressure has been brought to a high degree of efficiency.

"4. The accuracy of the gun is remarkable.

"5. The extreme range is probably about two miles. The effective range of projectiles in the trials witnessed by the Board has been from 1477 to 1868 yards.

"6. The power of the projectile has been determined only in a slight degree.

"7. The gun appears to be perfectly reliable in its action.

"8. The system is not a simple one. The gun does not require an expensive plant to manufacture and its cost should be moderate. Guns of this pattern can be made in any of the large towns of the country where there are machine shops and foundries.

"9. It is an important weapon for harbor defense.

"10. It is adapted to naval warfare whenever mortar fire can be used to advantage.

"11. A modification of it may be valuable to project torpedoes from ships when at short range.

"12. It is not expedient to adopt it as a part of the battery of ships of war until after the efficiency of the guns

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on board the dynamite cruiser, now building, has been ascertained and their performance afloat observed."

The dynamite cruiser is to have three 15-inch guns in lieu of the 10.5-inch originally named in the contract. These guns will be able to throw shell containing charges of 100, 200 and 600 pounds of explosive gelatine, the smaller charges to be fired from a sub-caliber device recently developed. The range of the heaviest shell will be the one mile called for in the contract, that of the lighter ones will be proportionately greater. The length of the gun has been shortened to 55 feet and designs have been prepared for still shorter ones. The 15-inch gun built for the Italian government, which is now being tested at Fort Lafayette, is but 40 feet in length.

There are now two rivals which have recently appeared in competition with Mefford's pneumatic gun. These are the "Maxim Dynamite Gun" and the "Rival Air Gun". Each inventor claims to be able to avoid the inconvenient and objectionable length of barrel which obtains in Mefford's gun. Instead of using compressed air alone, as the motor, Mr. Maxim uses a compressed mixture of air and some volatile hydrocarbon (gasoline, for example) the proportions being such as to produce the most perfect combustion. This mixture is used under one half the pressure of the air in Mefford's gun, and, after the projectile has been driven, by the expansive force of the compressed mixture, through one quarter or one half the length of the bore, the mixture is exploded and the pressure is thereby increased about eight fold. In the Rival Air-Gun or Aerial Torpedo Thrower the same end is sought to be obtained by using air pressures as high as 3000 lbs. per square inch and reducing the sensitiveness of the explosive by employing Graydon's system of loading the projectile. Both of these guns appear to be yet in embryo.

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In this resume no attempt has been made to point out the advantages or disadvantages of the various systems proposed, farther than what appears in the records quoted.

However we may briefly state that it has been shown that large torpedo charges of high explosives have been repeatedly, successfully and safely thrown to a distance of 1864 yards and detonated at that point by means of the Pneumatic Dynamite Gun, but that both the strongest advocate of this weapon and the Naval Board which witnessed the trials with it, disclaim that it in any way replaces powder guns. That then both economy and efficiency demand that experiments should be continued until we possess a perfected system for firing high explosive shell from our existing ordnance. That the experiments cited here tend to show that the successful solution of this very important problem is not improbable and that we are soon likely to effect it, and that with perhaps the exception of gun-cotton, we are more likely to find the explosive sought among the nitro-substitution compounds, which modern organic chemistry has revealed to us, than among the nitric esters. It is this fact which has led me, in this brief course of lectures, to dwell to such length on the theories, and to note so many of the new bodies which possess explosive properties or which may be employed in explosive mixtures.

In closing I trust it may not appear foreign to the subject if I present the following conditions of efficiency which I first set forth in 1885* and which my subsequent daily experience in the use of high explosives tends to confirm.

In determing the efficiency of high explosive projectiles against an armor-clad vessel, I assume that one of four

*Van Nostrands' Eng. Mag. 32, 1-8; 1885.

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effects may be produced, depending on the resistance of armor to penetration, and on the material, thickness of wall, profile, weight and velocity of the projectile.

1. The projectile may either penetrate the armor partially and explode in place, or pierce it completely and burst inside of the ship. This is the condition of greatest efficiency.

2. It may explode immediately upon impact, and before breaking up. Then the explosive will exert the energy which it develops through explosion in a resisting receptacle.

3. It may rebound before exploding. Then the effect will be reduced by the interposed cushion of air.

4. It may break up on impact before the explosion takes place. Then the energy of the explosive will be simply that which it developes when exploded unconfined.

The resistance of an armor to penetration depends upon its hardness, its tensile strength (that due to bolting as well as that inherent in the metal itself), and its inertia. The latter is augmented by the thickness and weight of the armor, and by the rigid system of bracing which now obtains in practice.

Reference book, *Proc. U. S. Naval Institute.*

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PRACTICAL EXERCISES IN EXPLOSIVES.

MADE BY

CLASS UNDER INSTRUCTION,

MAY TO AUGUST, 1888.

COMPARISON OF EXPLOSIVES WHEN FIRED UNDER WATER.

Exercise torpedo Pattern C filled with gunpowder and exploded by D. E. igniter.

Exercise torpedo Pattern C filled with gunpowder and exploded by service detonator.

Exercise torpedo Pattern C filled with picric powder and exploded by D. E. igniter.

Exercise torpedo Pattern C filled with picric powder and exploded by service detonator.

Exercise torpedo Pattern C filled with rack-a-rock and exploded by D. E. igniter

Exercise torpedo Pattern C filled with rack-a-rock and exploded by service detonator.

Exercise torpedo Pattern C filled with dynamite No. 1 and exploded by D. E. igniter.

Exercise torpedo Pattern C filled with dynamite No. 1 and exploded by service detonator.

Exercise torpedo Pattern C filled with gun-cotton and exploded by D. E. igniter.

Exercise torpedo Pattern C filled with gun-cotton and exploded by service detonator.

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Exercise torpedo Pattern C filled with rack-a-rock and exploded by *brass* igniter.

Exercise torpedo Pattern C filled with dynamite No. 1 and exploded by *brass* igniter.

Exercise torpedo Pattern C filled with gun-cotton and exploded by *brass* igniter.

The torpedoes were attached to a Harvey bouy placed at a distance of 200 feet from the firing point, an anchor was attached to each torpedo and the latter were slung so as to be immersed 10 feet beneath the surface, in five fathoms of water. The effect produced upon the water; the height, form and dimensions of the crater; the acoustic and other attending phenomena; and the appearance of the material recovered, were all noted.

FULMINATE OF MERCURY.

Manufactured fulminate of mercury.

Charged service detonators with fulminate.

Fired a blasting cap with Bickford's fuse after determining speed of combustion of fuse.

Fired a wooden D. E. igniter in an empty Exercise torpedo case.

Fired a wooden D. E. igniter in an Exercise torpedo case filled with damp sand.

Fired a service detonator in an empty Exercise torpedo case.

Fired a service detonator in a block of oak $3\frac{1}{2} \times 3\frac{1}{2} \times 3$ inches.

GUN-COTTON.

Superintended manufacture.

Burned a 50 pound box of wet gun-cotton in a bonfire.

Extracted burning discs from bonfire and extinguished the flames by means of water and by rolling on the earth.

Detonated partially burned discs.

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Detonated dry gun-cotton with service detonators and Farmer's machine and with Bickford's fuse and blasting caps.

Detonated wet gun-cotton, in the open, by means of dry primers.

Inspected Chemical Box (No. 16 of G. C. Torpedo Outfit) packed ready for issue.

Made monthly inspection of dry primers.

Inspected Service G. C. Torpedoes Pattern D, packed ready for issue, using contents of Chemical Box.

Observed method of making heat test.

" " " " " solubility test.

" " " " " alkalinity test.

" " " " " nitrometer test.

NITRO–GLYCERINE AND DYNAMITE.

Observed method of manufacture by Vonges' method.

Inspected apparatus for manufacture by Hill's method.

Tested nitro-glycerine and dynamite for acidity.

Tested dynamite to prove presence of nitro-glycerine.

Fired Atlas powder No, 1, in the open by both service detonators and Farmer's machine, and blasting caps and Bickford's fuse.

SPRINGING MINES.

Two experiments were made in earth bank at north end of Goat Island. In one gun-cotton charges were used. In the other Atlas powder charges were used.

DESTRUCTION OF MATERIAL.

Stout spruce timbers 10 × 4¾ inches were erected at north end of Goat Island and they were cut off by charges of gun-cotton, both wet and dry, and of Atlas powder No. 1. The charges were calculated for the dimensions of the timbers, were fastened upon their faces, and were either tamped with wet sod or untamped.

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The same experiments were repeated using wrought iron I beams 5 inches on the face, 9 inches web and $\frac{5}{8}$ inch thickness of web.

REMOVAL OF OBSTRUCTIONS.

A wreck at Rose Island was destroyed by means of gun-cotton torpedoes. The mass and location of the charges used were determined by previous inspection and measurement of wreck.

EXPLOSIONS BY INFLUENCE.

Seven $\frac{1}{2}$ inch discs of gun-cotton were placed upon an armor plate, the discs being separated from one another by distances varying from $\frac{1}{2}$ to $1\frac{1}{2}$ inches and the central disc was detonated.

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PRACTICAL EXERCISES.

BEFORE

BOARD OF VISITORS,

JULY 30TH, 31ST, 1888.

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1. Conduct the Board through the Gun-Cotton Factory and explain the various processes employed in making gun-cotton.

2. With the apparatus before you, explain the process employed at this Station for making nitro-glycerine.

3. With the apparatus before you, explain the method of applying the "heat test" for the stability of gun-cotton.

4. With the apparatus before you, describe the method of making the solubility test for gun-cotton.

5. Demonstrate the way in which the "monthly test" for dry gun-cotton primers is to be made, using several jars of primers.

6. Explain how fulminate of mercury is made, and service detonators are filled.

7. Show by exploding in an empty exercise torpedo case, a block of wood, and a can of water, the power of a service detonator.

8. Detonate a disc of dry gun-cotton freely exposed on an iron plate. Repeat the experiment, using one disc of wet and one of dry gun-cotton.

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9. Using six half-inch discs of dry gun-cotton, show what is meant by the term "explosion by influence".

10. Place a box of wet gun-cotton in a bonfire, and, after it is partially consumed, remove some of the unconsumed discs and detonate them on an iron plate by means of a dry primer. Set fire to a dry disc and extinguish it by means of water.

11. Cut a plank by means of a superficial charge of gun-cotton.

12. Detonate a dynamite cartridge by means of a Bickford fuse and blasting cap, having previously determined the rate at which the fuse burns.

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EXAMINATION

QUESTIONS IN EXPLOSIVES,

SUMMER OF 1888.

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1. What is Bellite and how is it made? What advantages are claimed for it?

2. Describe the process of making fulminate of mercury and of filling service detonators as carried on at the Torpedo Station. What precautions must be taken in the manufacture and use of detonators to insure success in use? What position does the detonator hold in any explosive system such as a torpedo or mine?

3. What advantage does gun-cotton possess as a naval explosive? To what has the feeling of insecurity regarding the stability of gun-cotton, which has existed in the past, been due? What methods are pursued for testing military gun-cotton in order to determine if it is in suitable condition for issue to the service or for storage on shipboard?

4. Describe the process of manufacture of service gun-cotton as conducted at the Torpedo Station. In what form, condition and containers is it issued to the service?

5. What advantage would accrue if our present service guns could be safely used under service conditions to project shell filled with high explosives? What are the

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prospects of this result being attained? Cite some experiments which have been made looking to this result. What is the chief obstacle to success? What are the conditions which determine the efficiency of such shell when used against armor?

6. What are the Sprengel mixtures? Cite two examples of such, giving composition and mode of use. Has either of them been successfully used in practice?

7. What is dynamite? How is it made, used, tested, and handled, especially when frozen? How is it exploded in the arts?

8. What is explosive gelatine and how is it made? For what purpose is it proposed to use it in war? What advantages and disadvantages does it possess for this purpose?

9. Show the relation of combustion to explosion and detonation. How is the great explosiveness of nitrogen chloride explained? What light has the study of the explosive amides and amines thrown upon the properties of the explosive compounds in general?

10. What is Cocoa Powder? Point out how the advantages of a high initial velocity with a low pressure are secured. What is the probable source of the charcoal used in the German Cocoa?

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PLATES.

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PLATE 1.

FIRST BOILING TUB.

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PLATE 1.

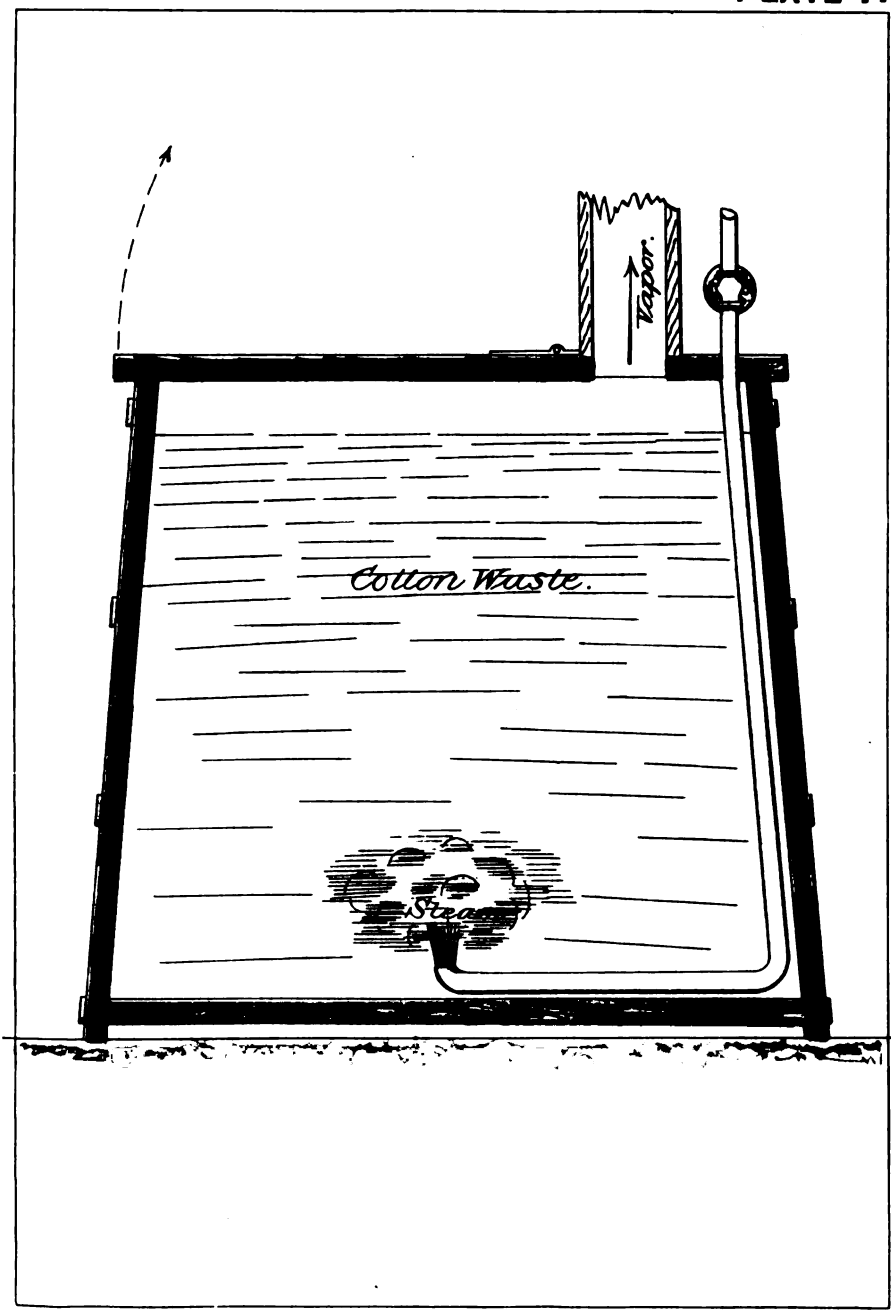

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PLATE 2.

CENTRIFUGAL WRINGER.

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PLATE 2.

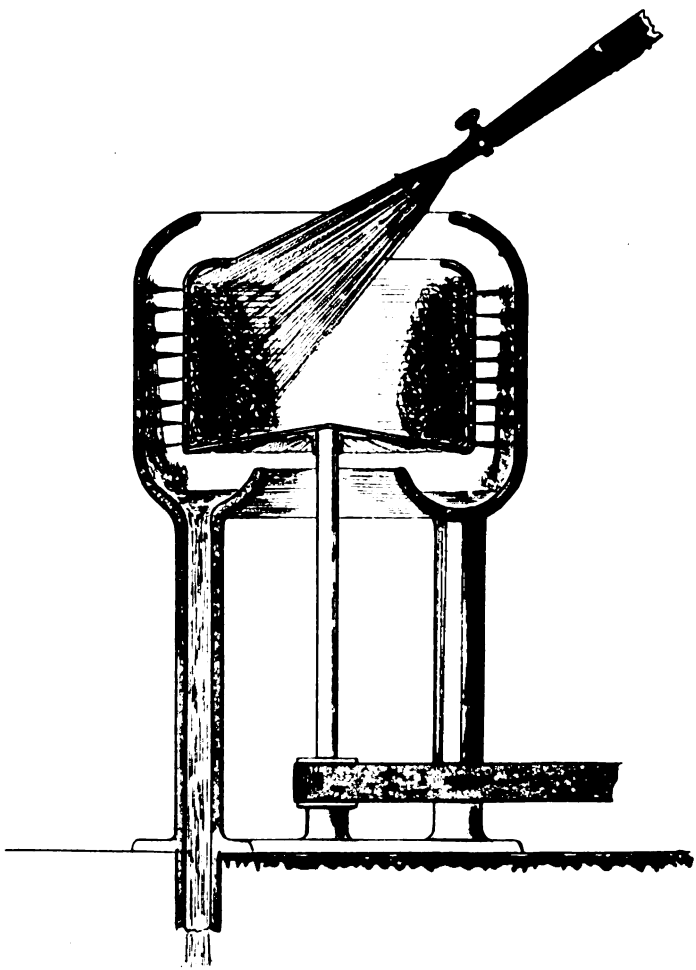

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PLATE 3.

PICKER.

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PLATE 3.

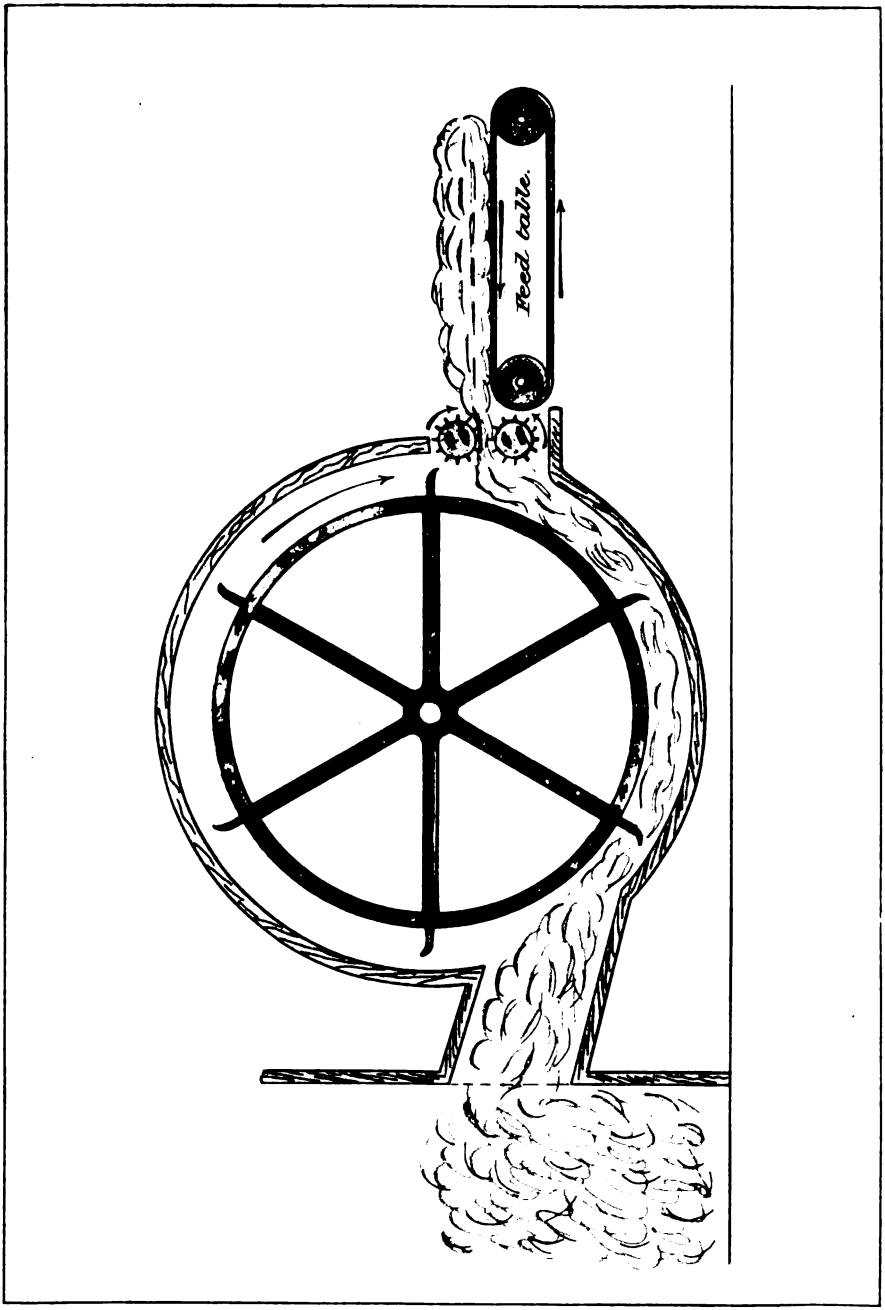

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PLATE 4.

FINAL DRYER.

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PLATE 4.

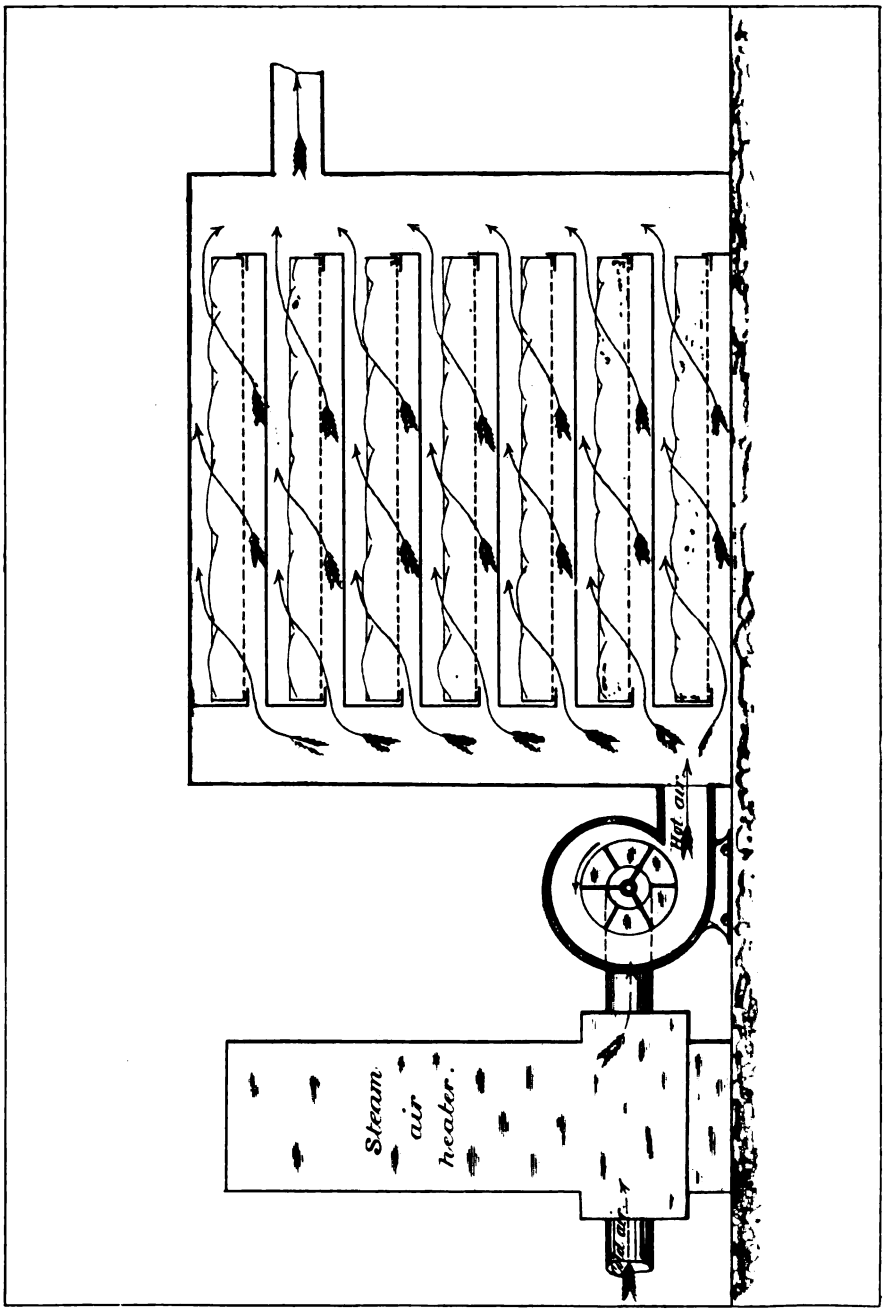

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PLATE 5.

1. DIPPING TROUGH.
2. DIGESTION POT.
3. LEVER PRESS.
4. HAND PRESS.
5. FORK.

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Plate 5.

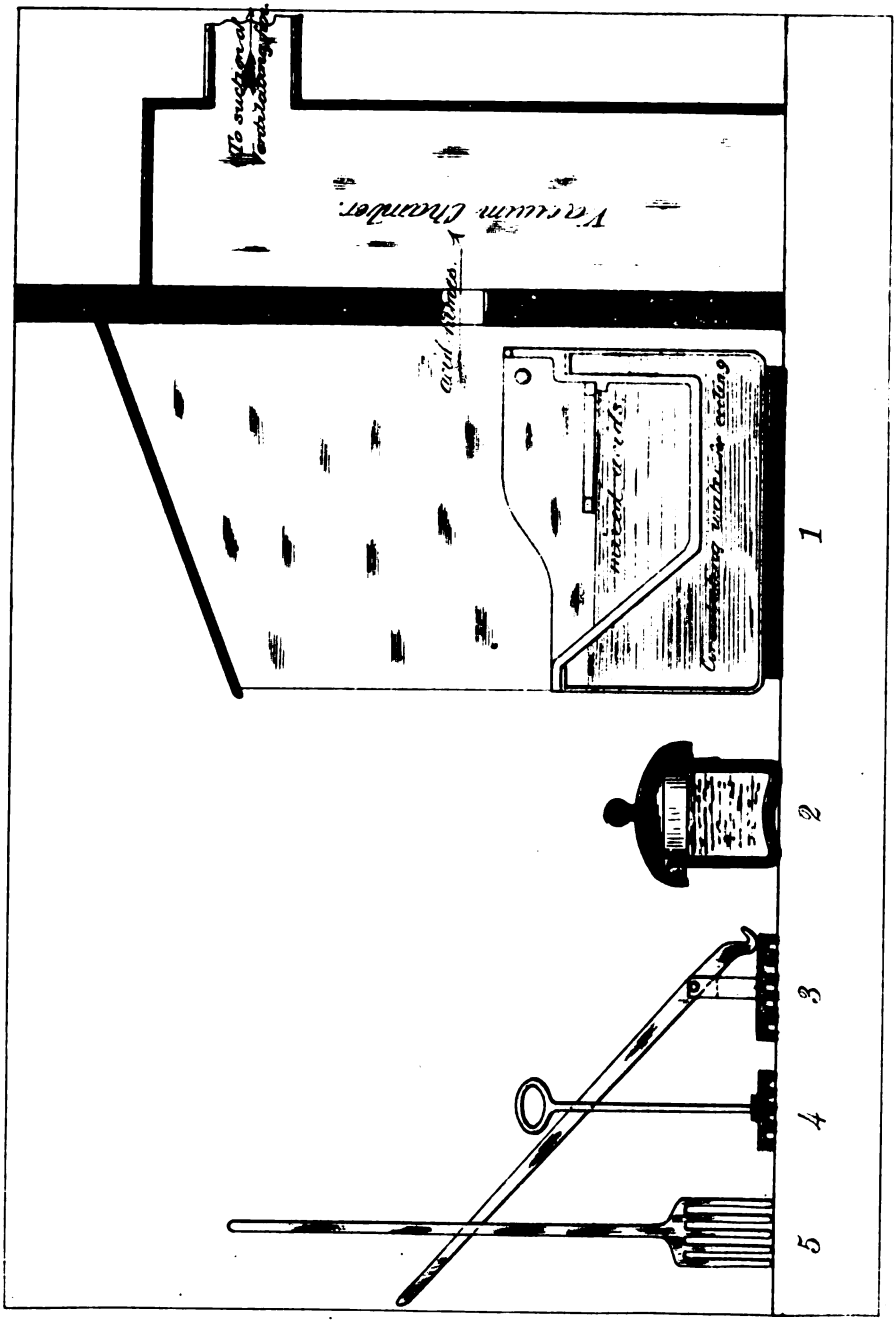

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PLATE 2.

CENTRIFUGAL WRINGER.

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PLATE 2.

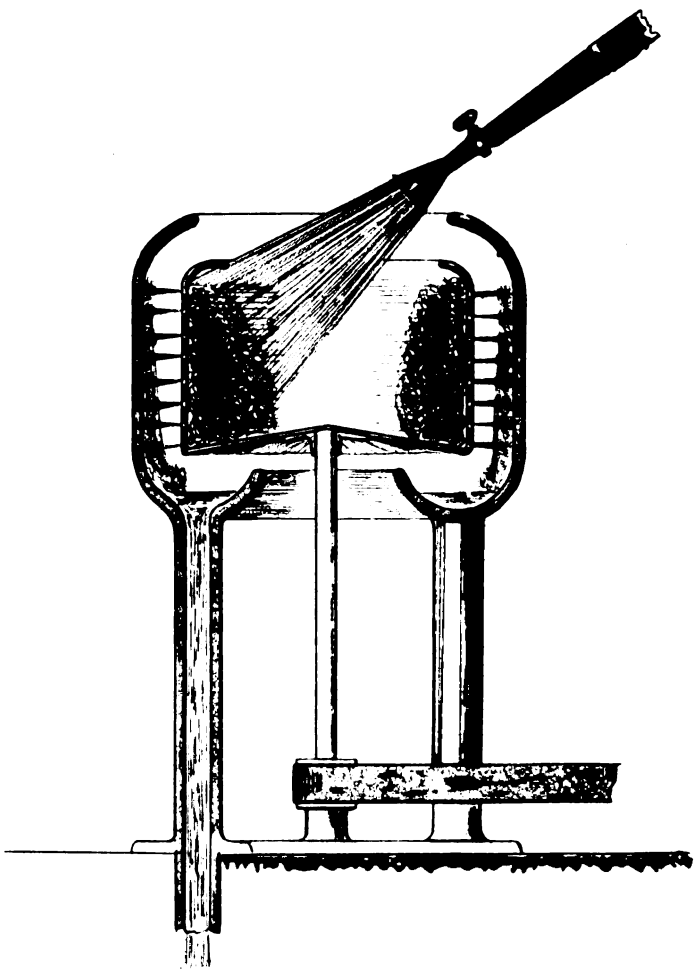

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PLATE 3.

PICKER.

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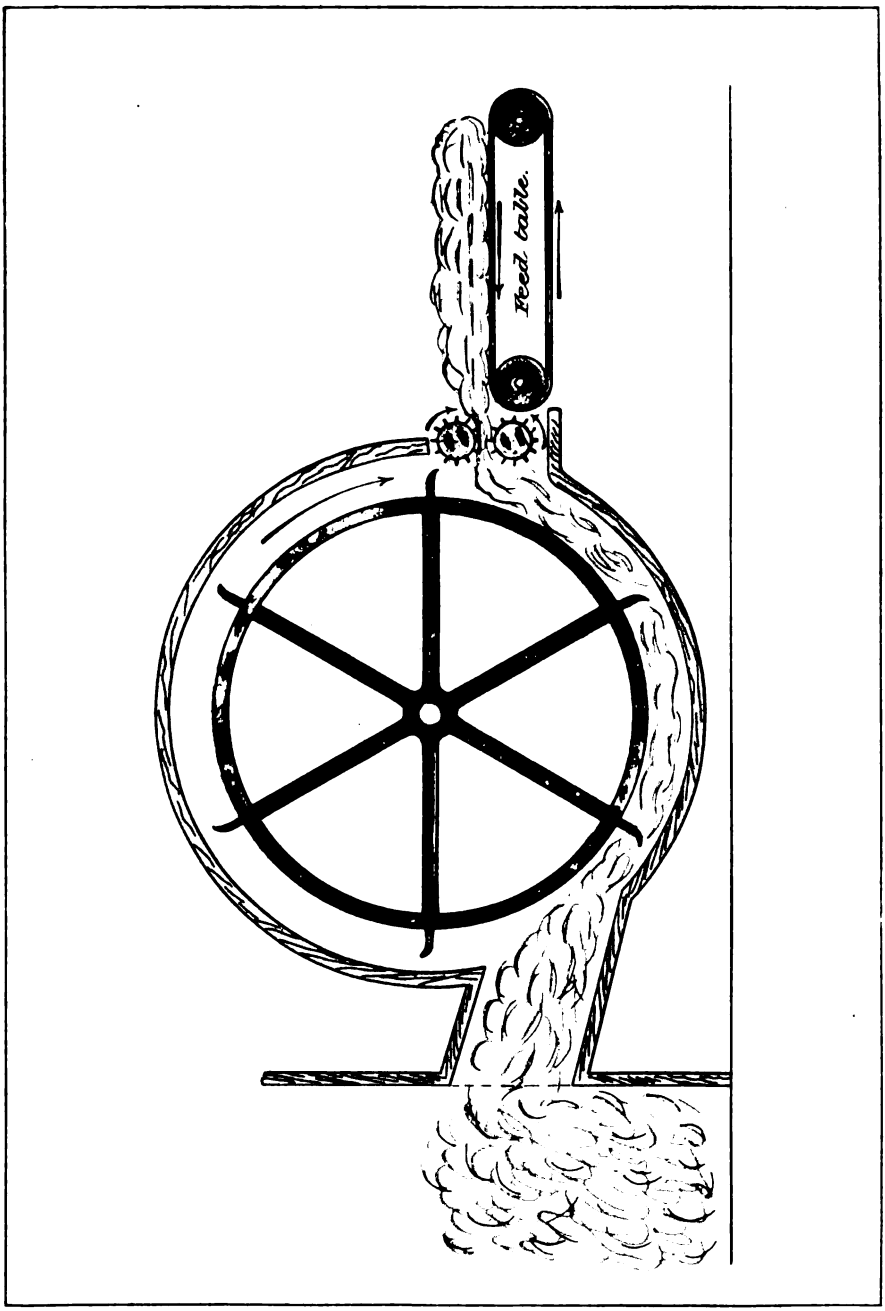

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PLATE 4.

FINAL DRYER.

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FINAL DRYER.

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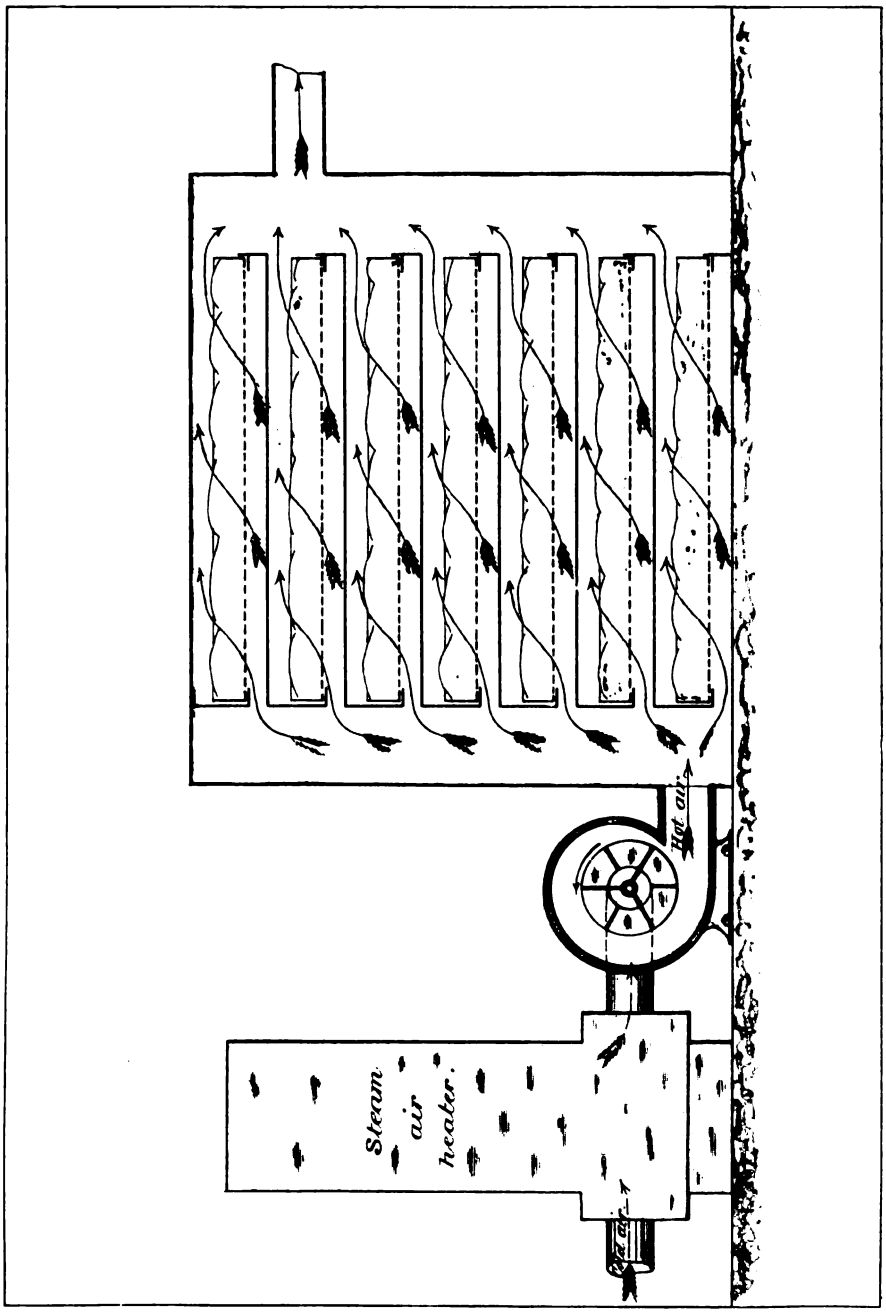

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PLATE 5.

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PLATE 5.

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PLATE 6.

ACID WRINGER.

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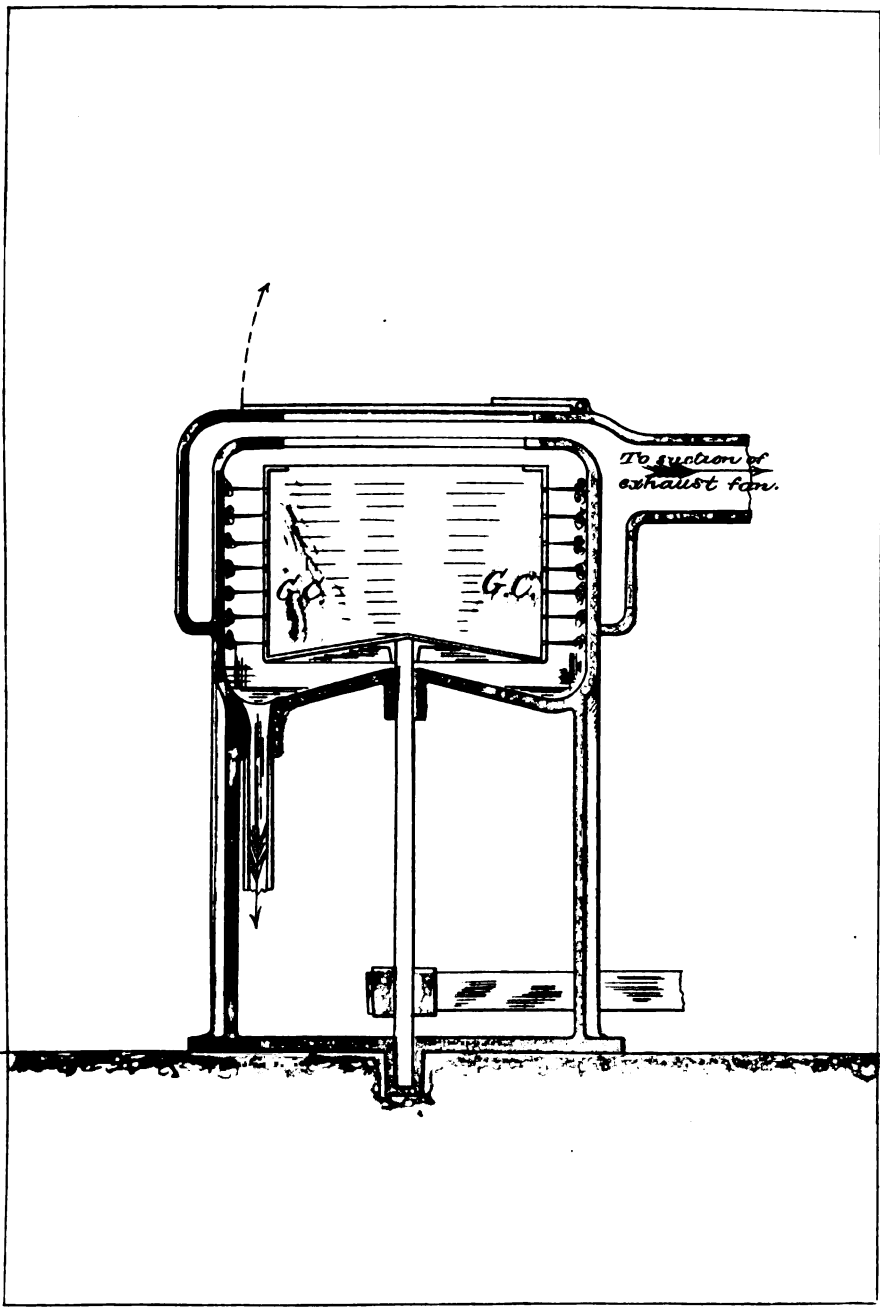

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PLATE 7.

IMMERSION TUB.

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PLATE 7.

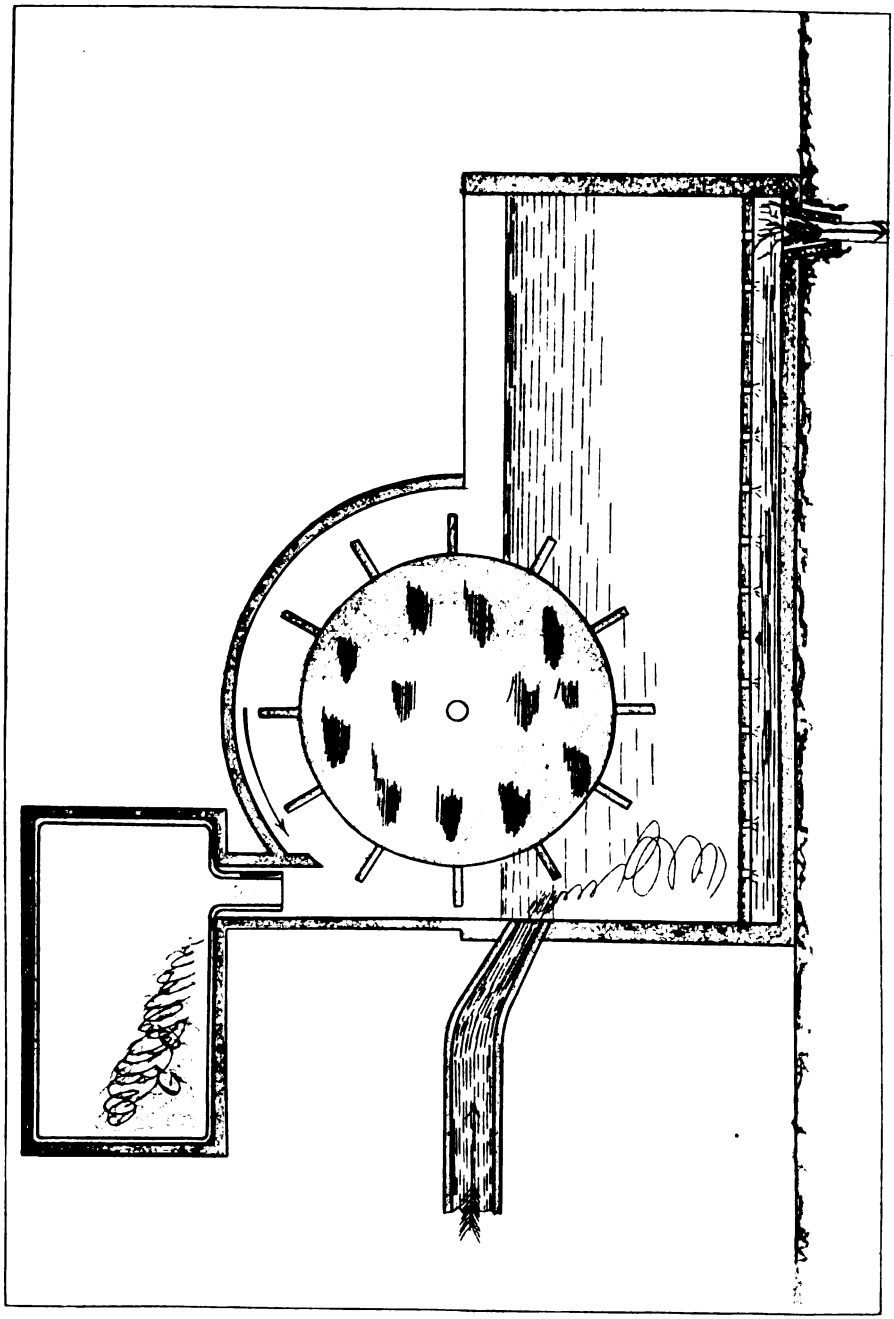

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PLATE 8.

SECOND BOILING TUB.

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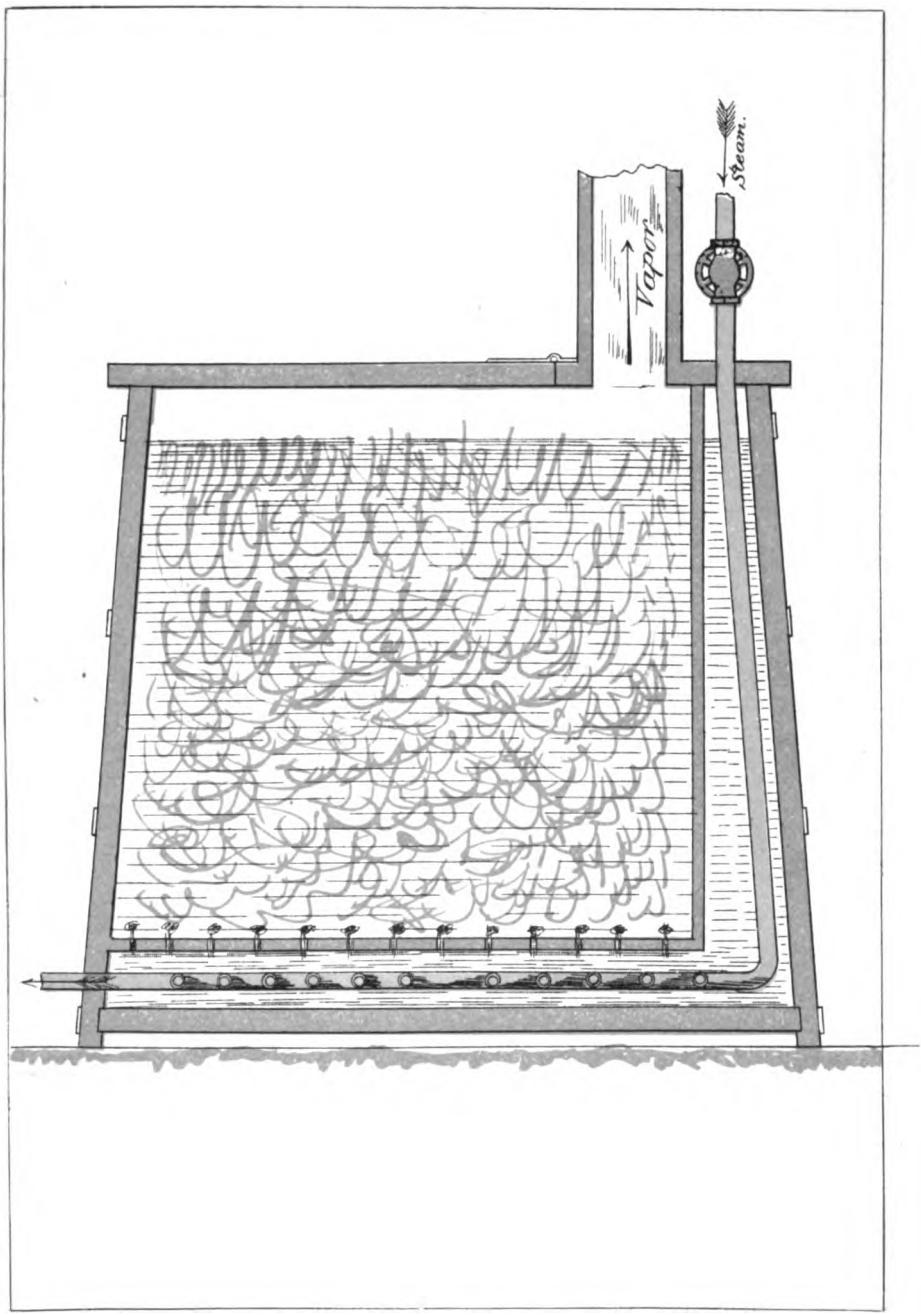

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PLATE 9.

PULPER.

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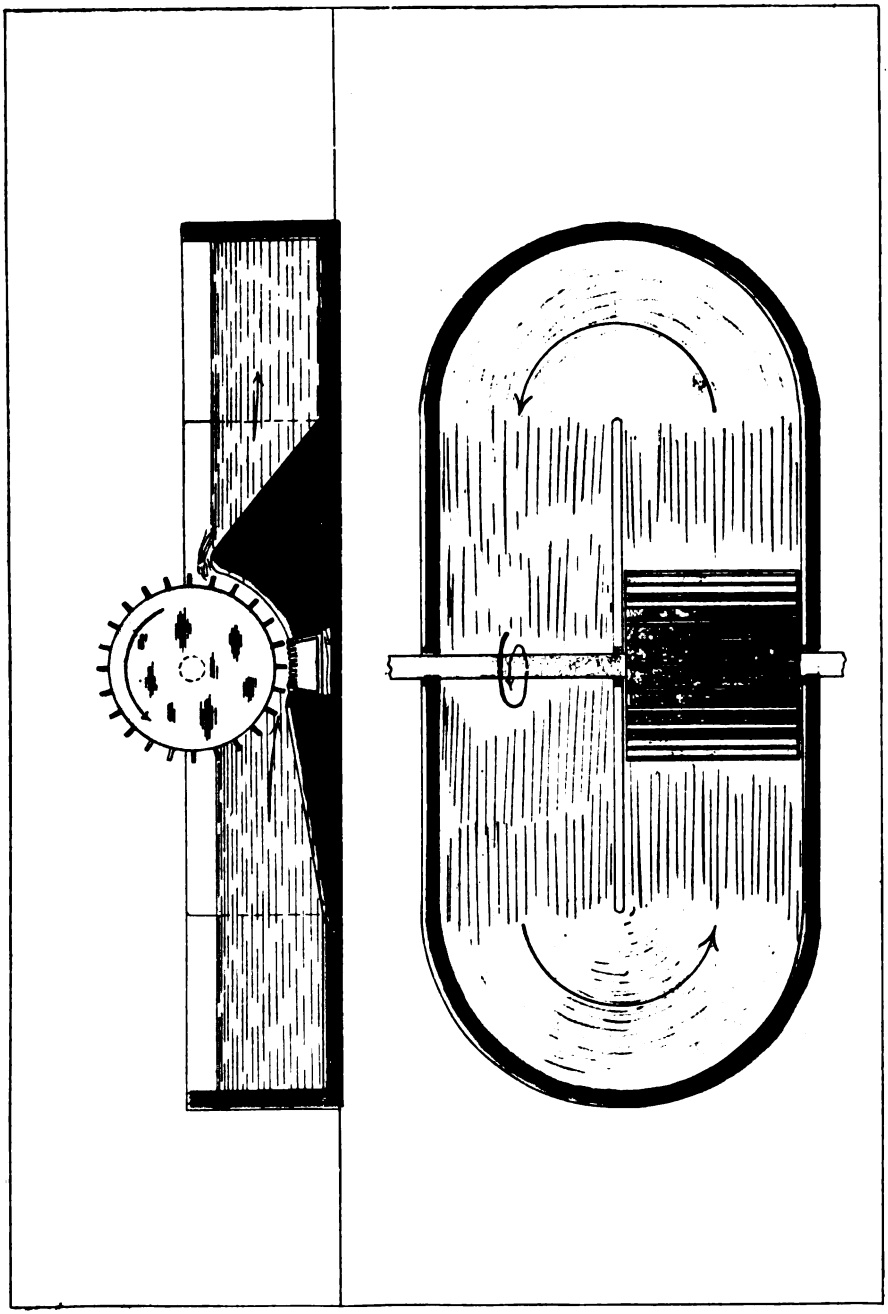

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PLATE 10.

POACHER.

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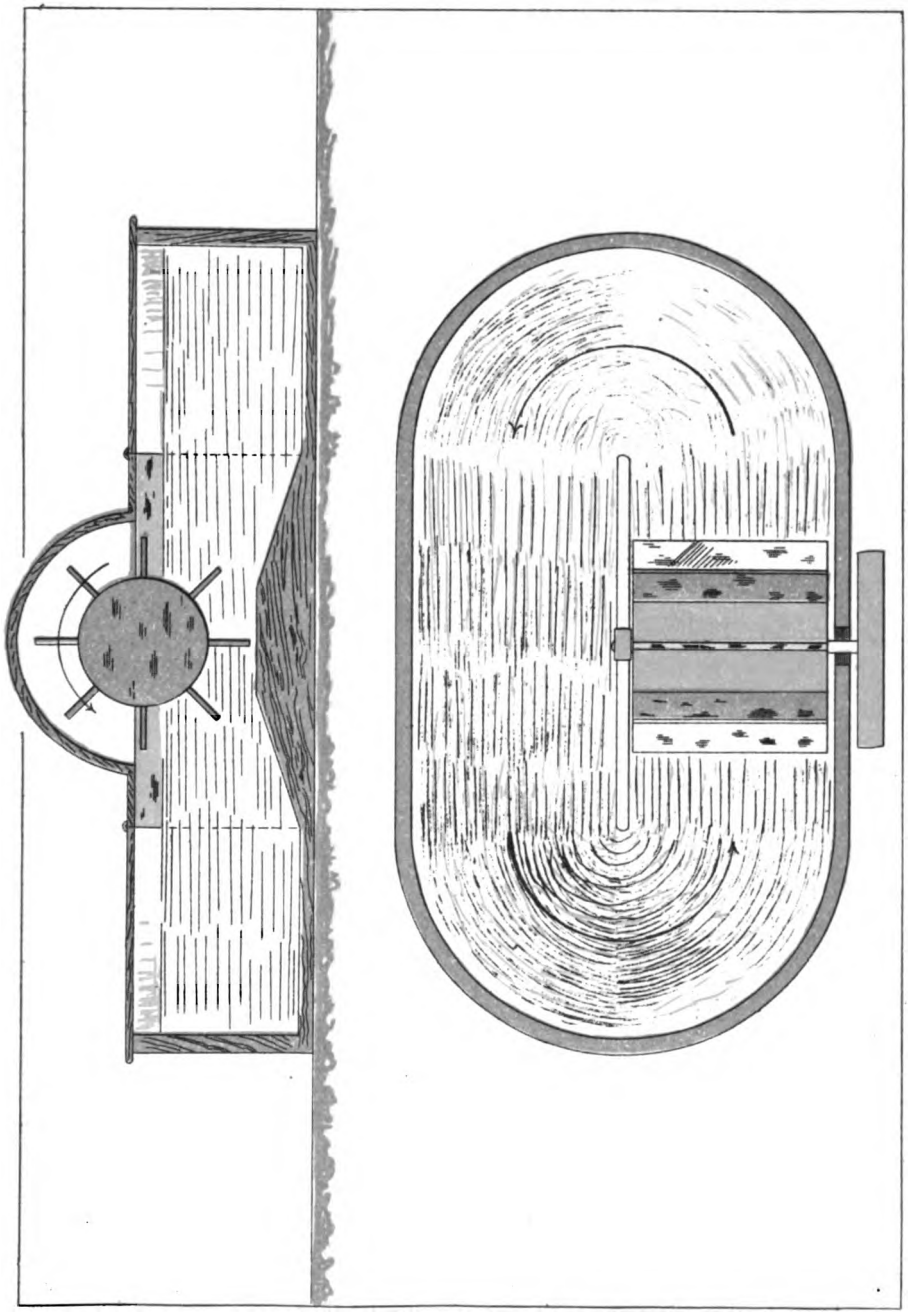

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PLATE 11.

MOLDING PRESS.

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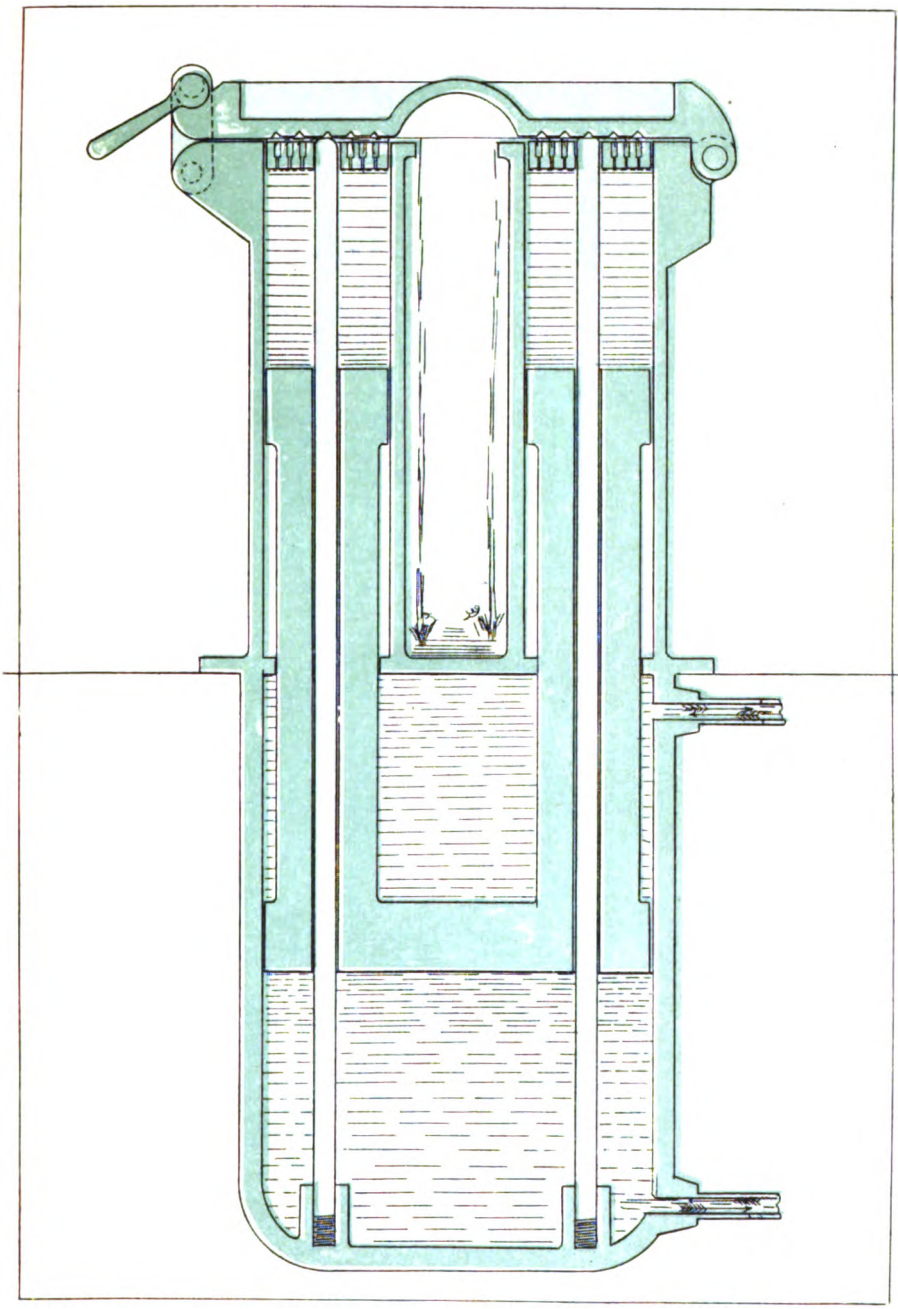

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PLATE 12.

FINAL PRESS.

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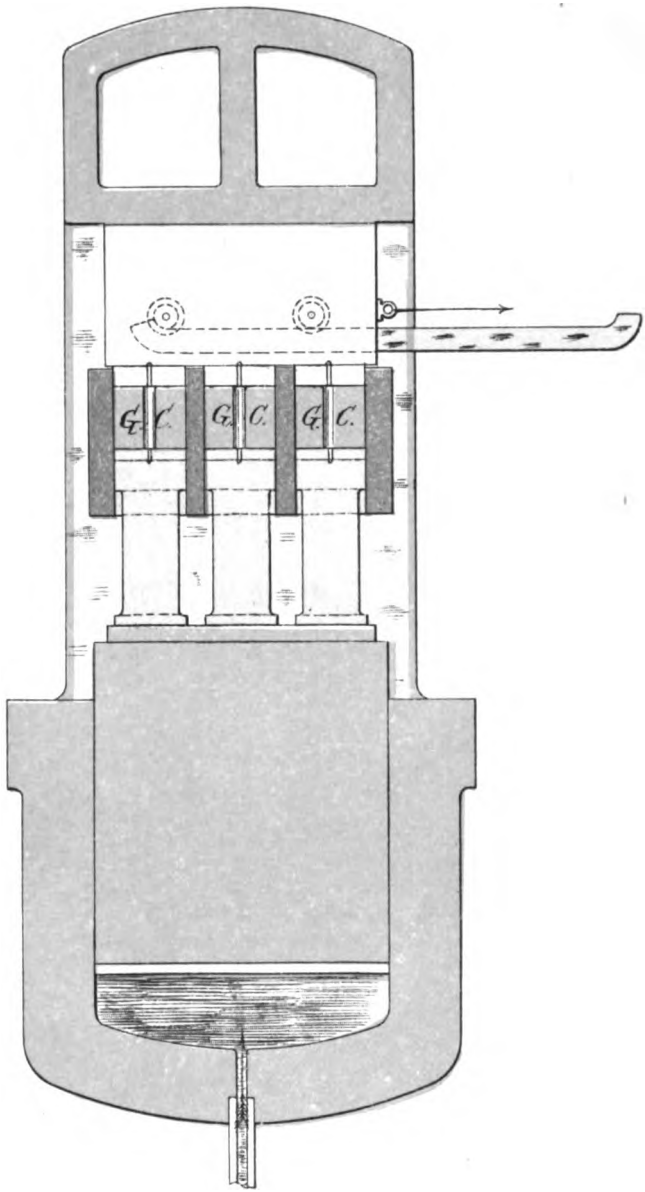

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PLATE 10.

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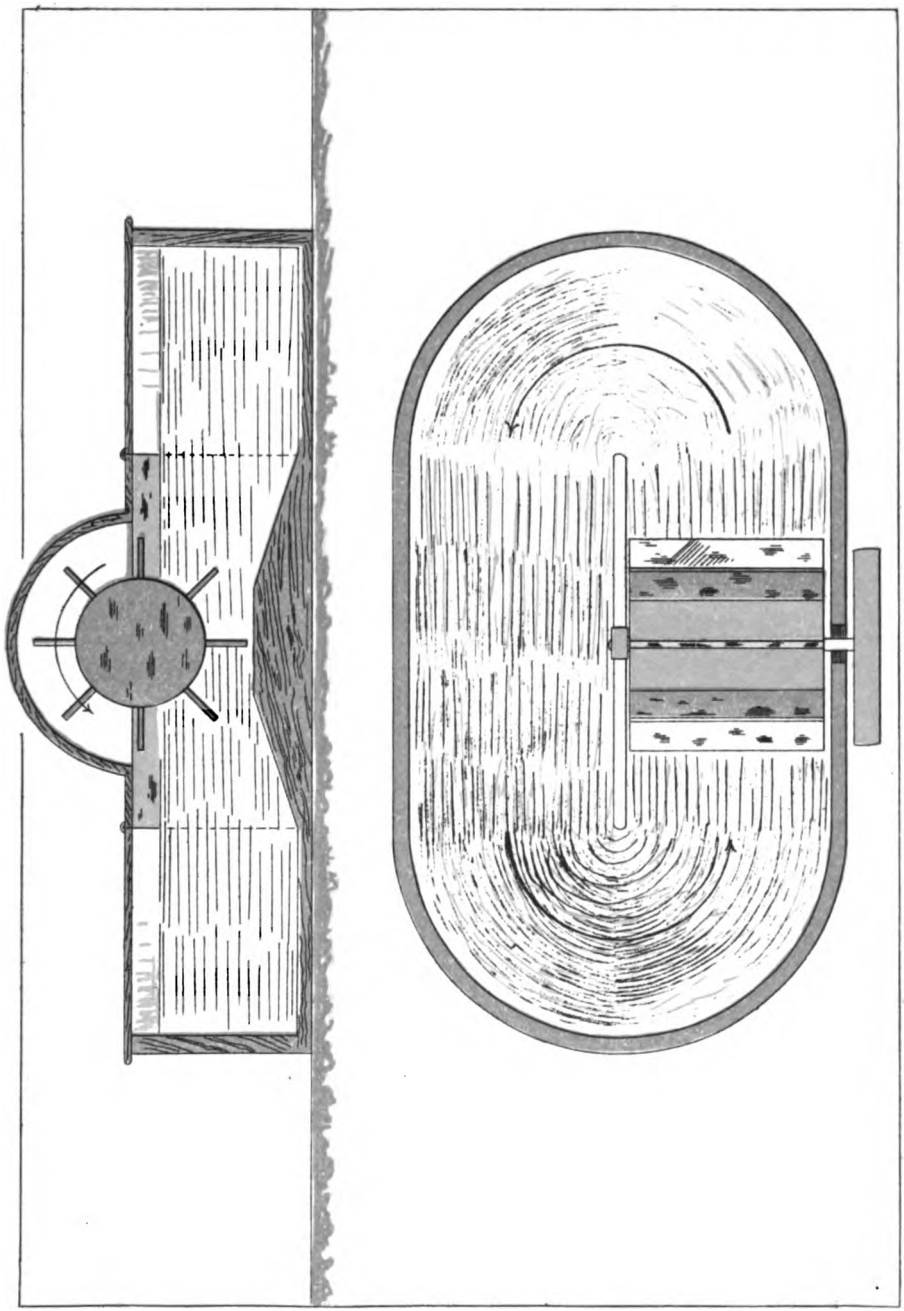

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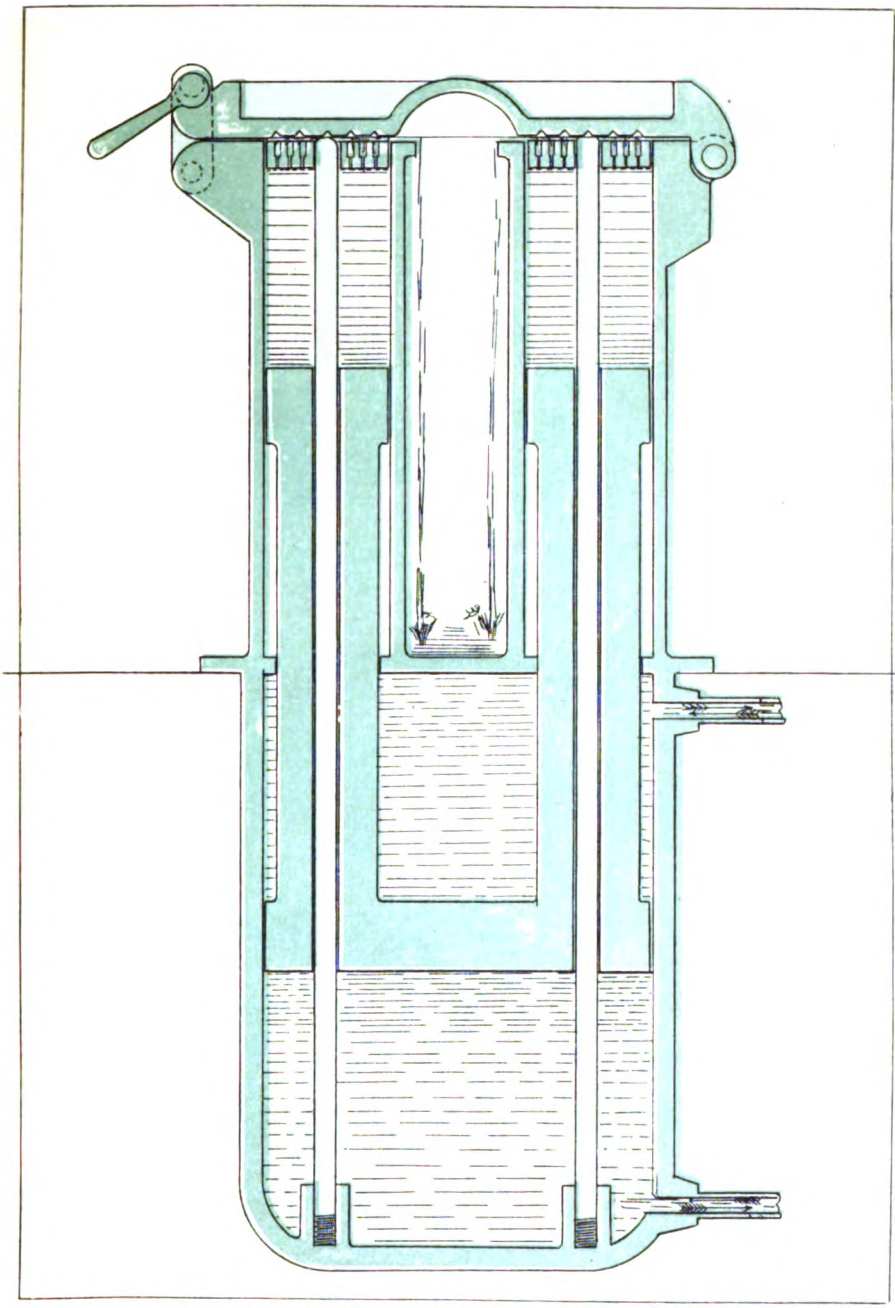

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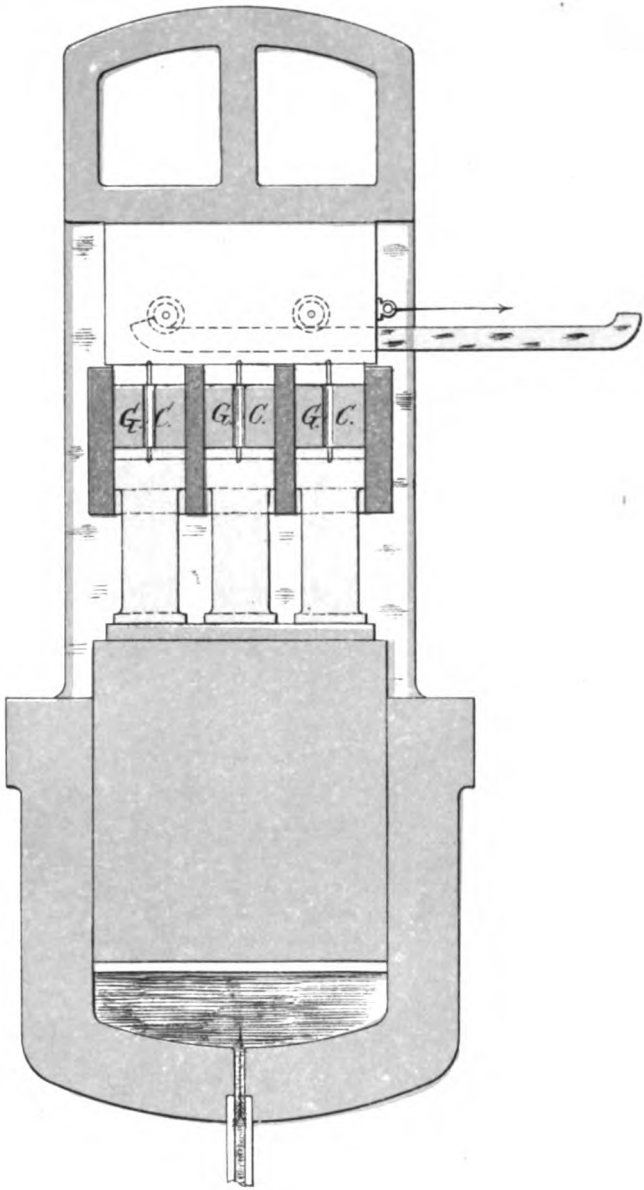

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PLATE 1.

FIRST BOILING TUB.

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PLATE 1.

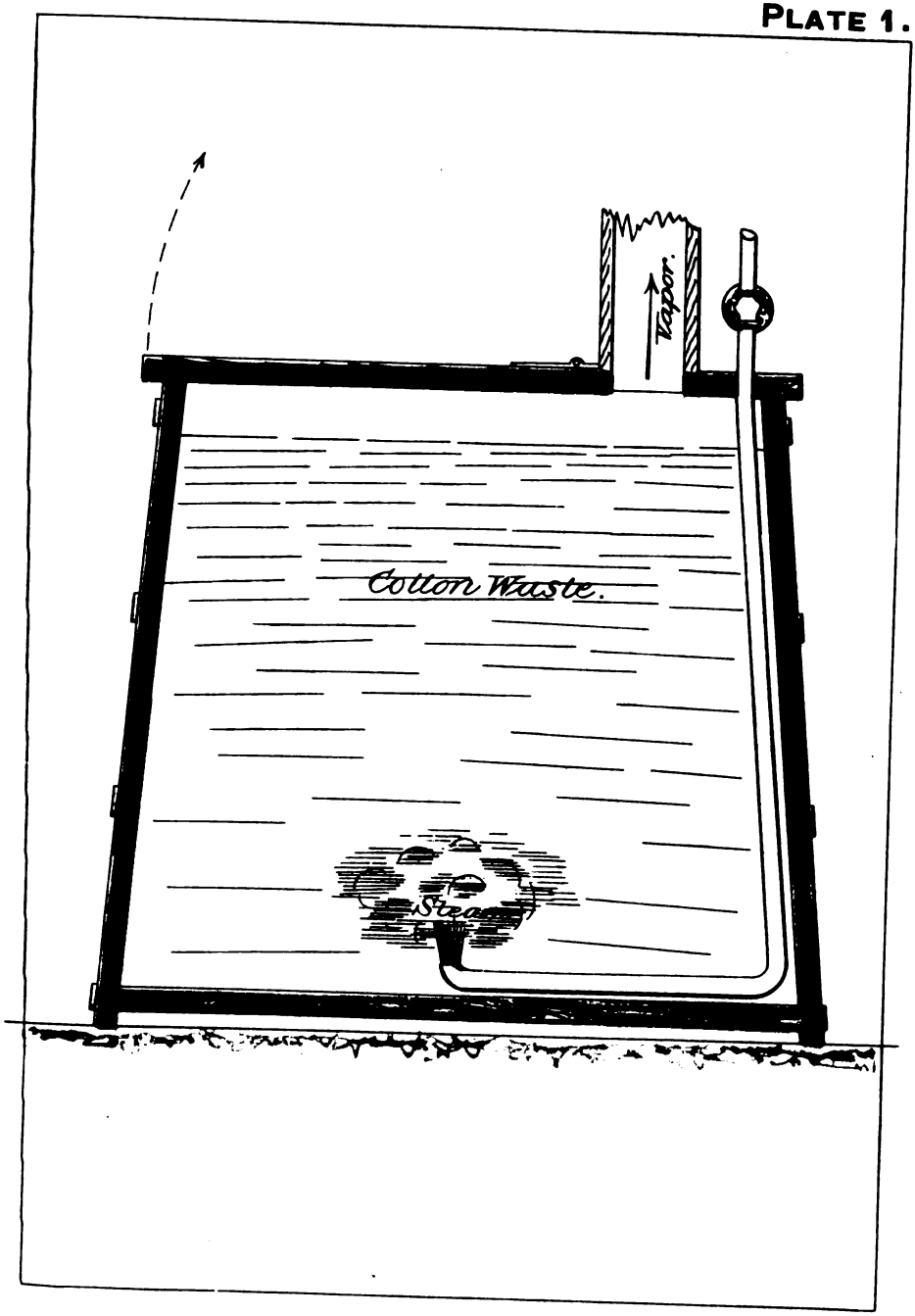

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PLATE 2.

CENTRIFUGAL WRINGER.

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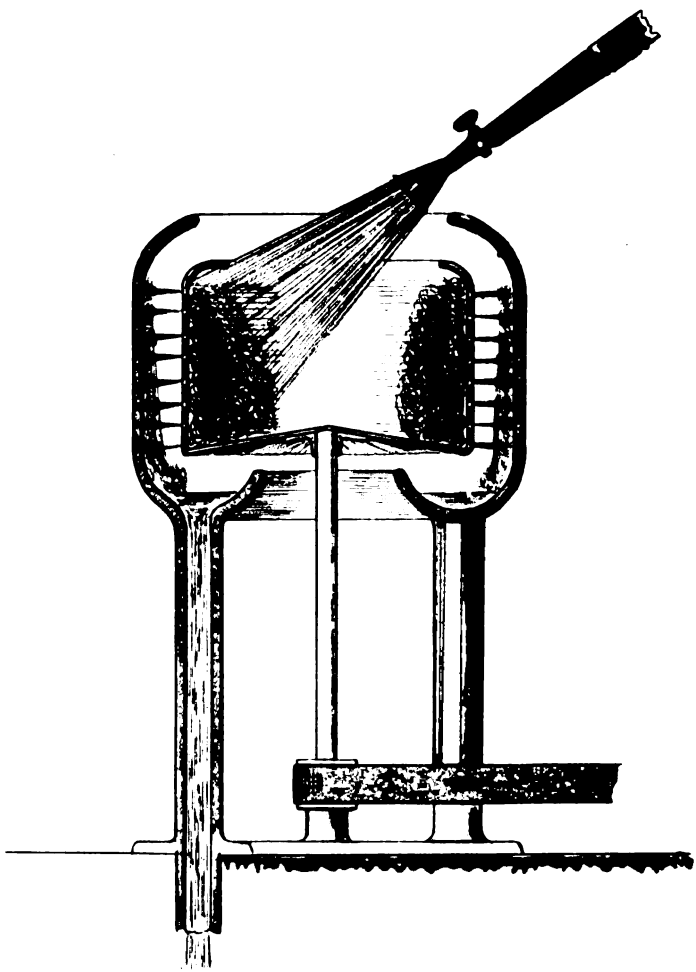

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PLATE 3.

PICKER.

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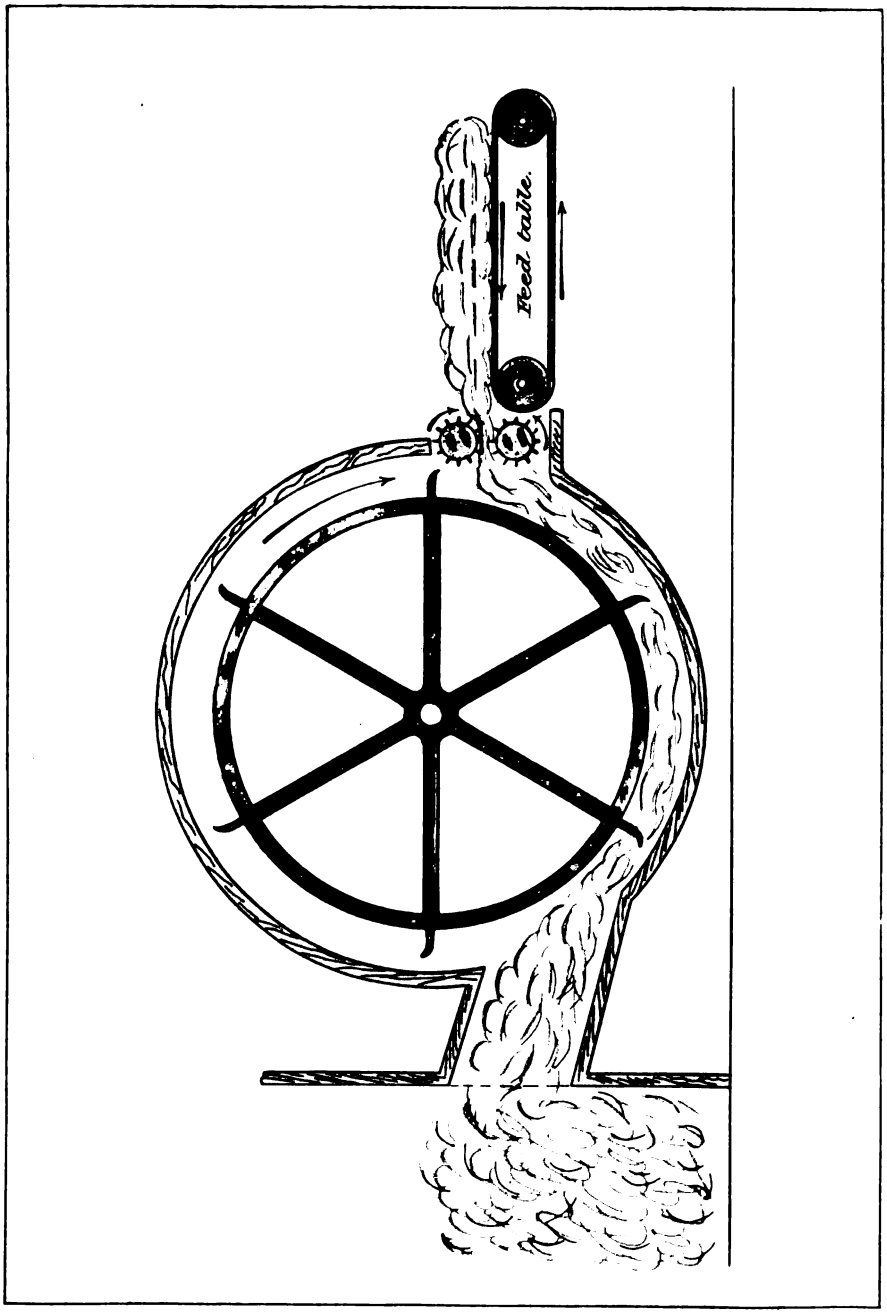

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PLATE 4.

FINAL DRYER.

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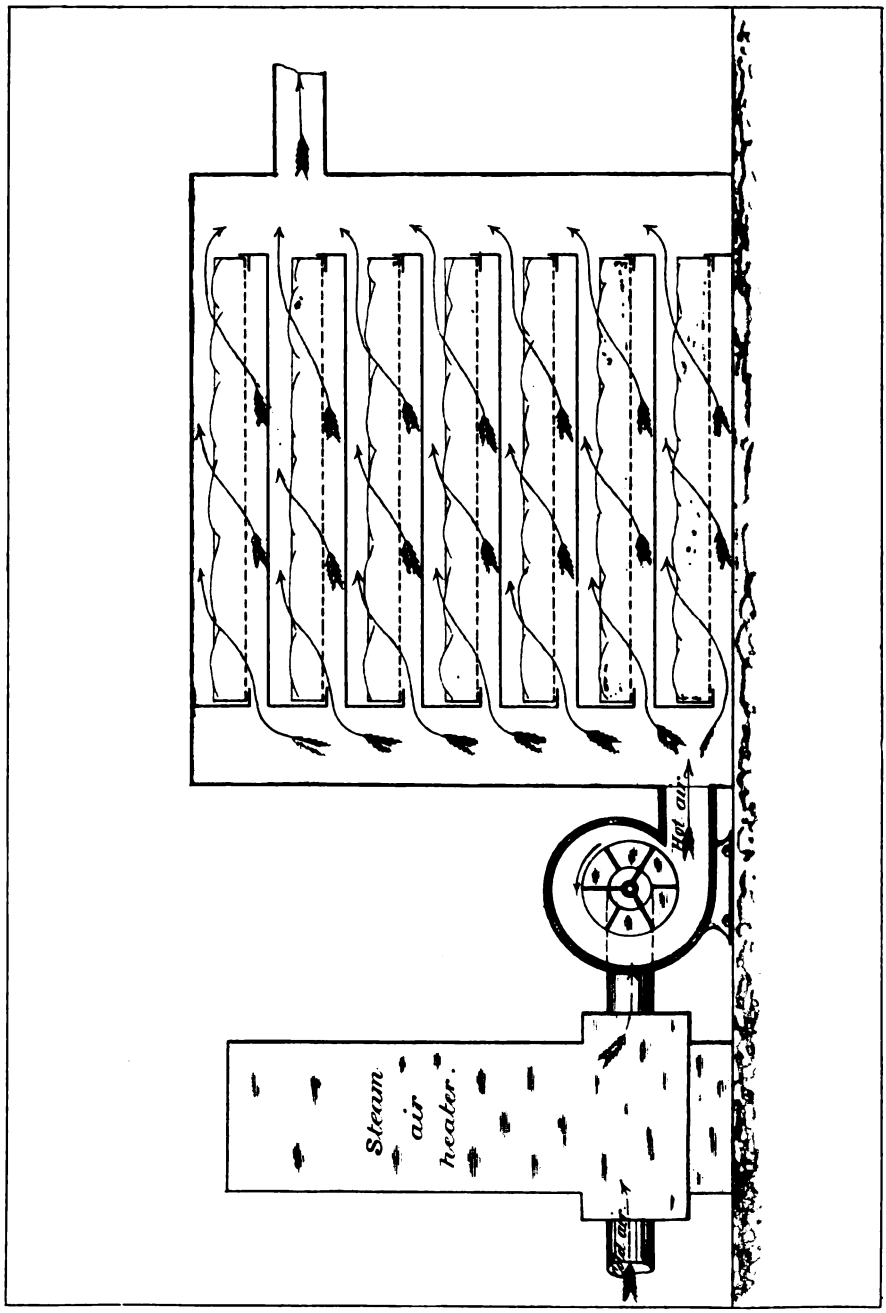

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PLATE 5.

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PLATE 1.

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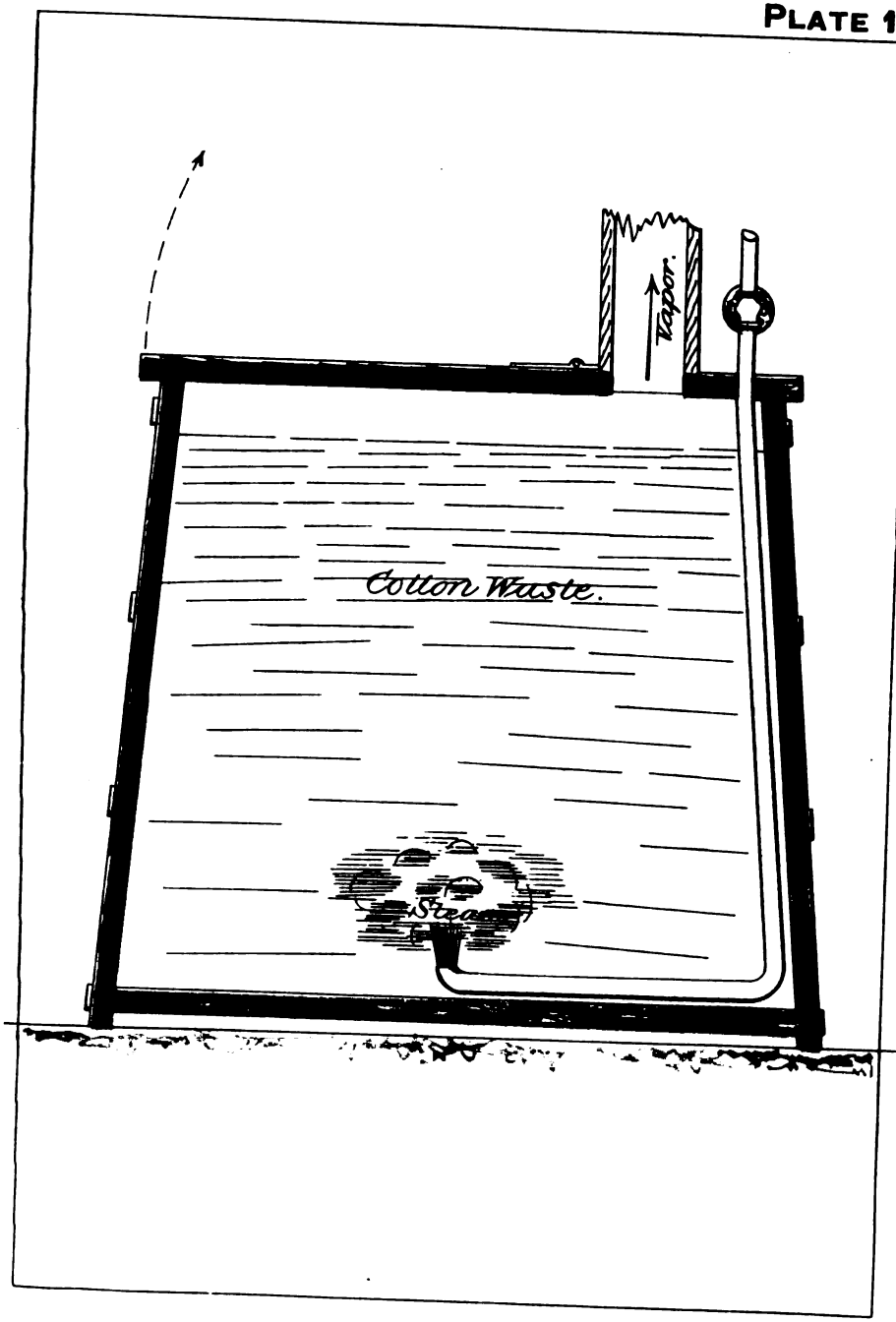

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PLATE 2.

CENTRIFUGAL WRINGER.

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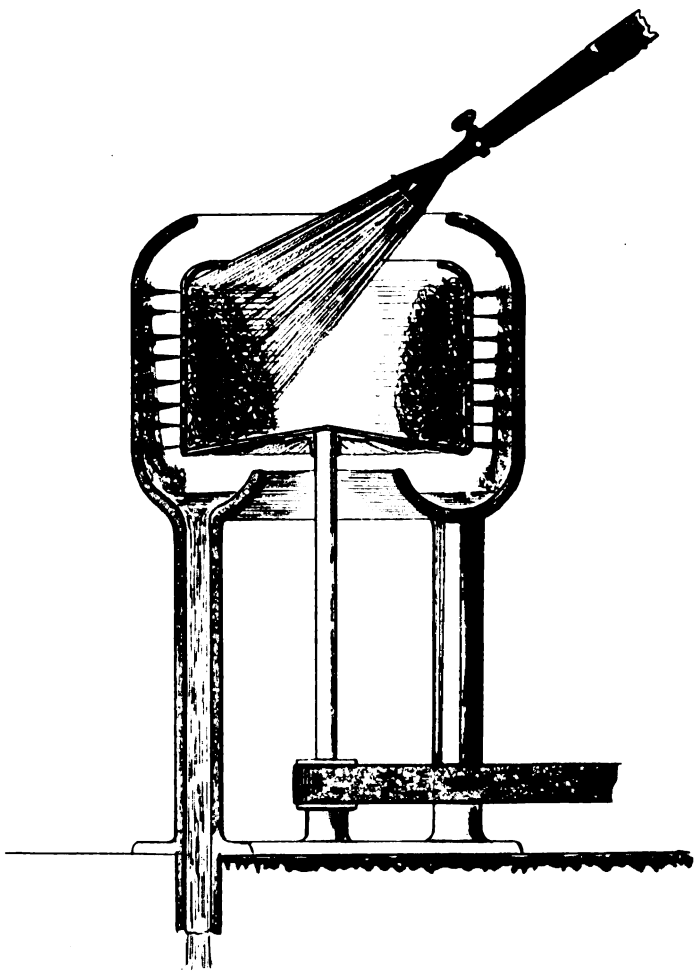

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PICKER.

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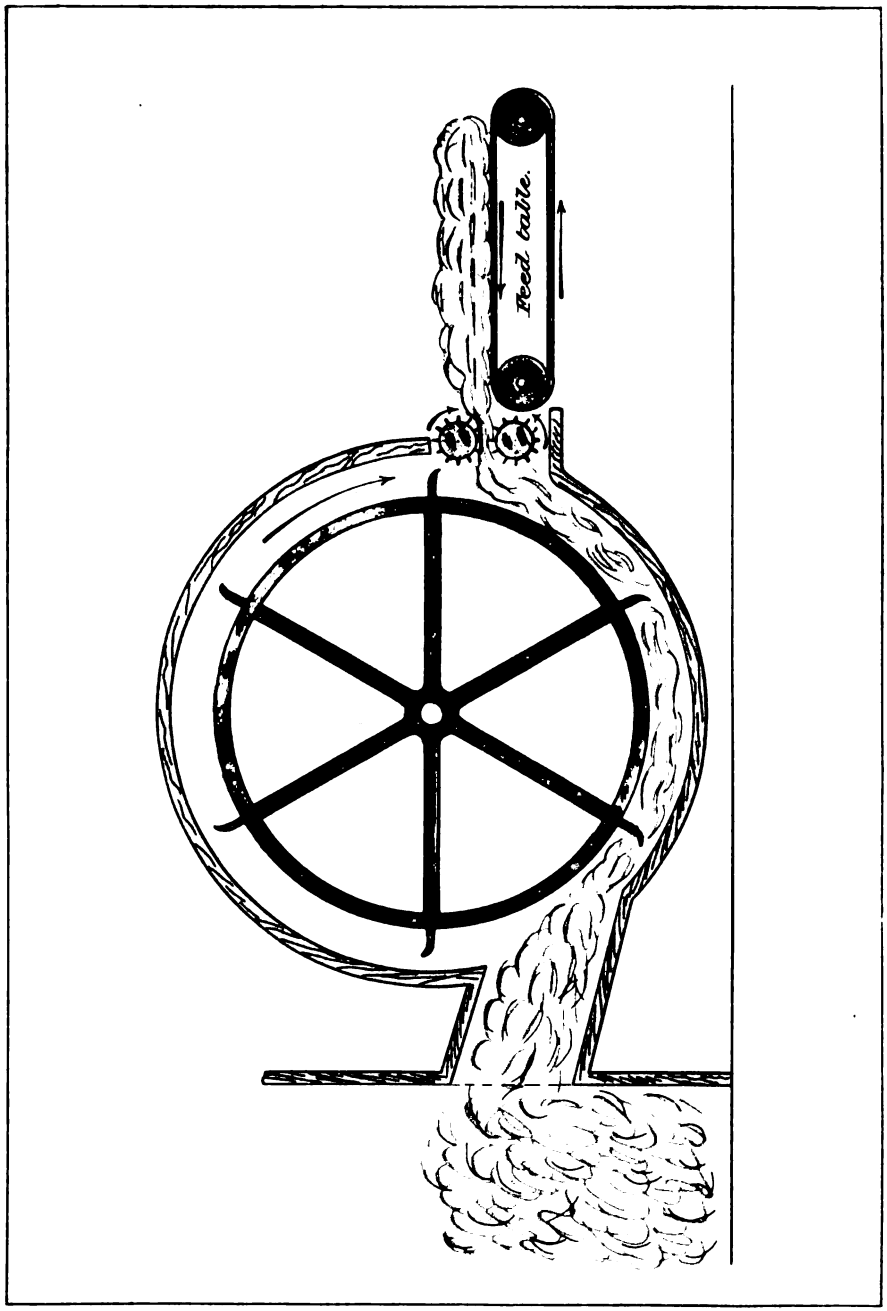

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PLATE 4.

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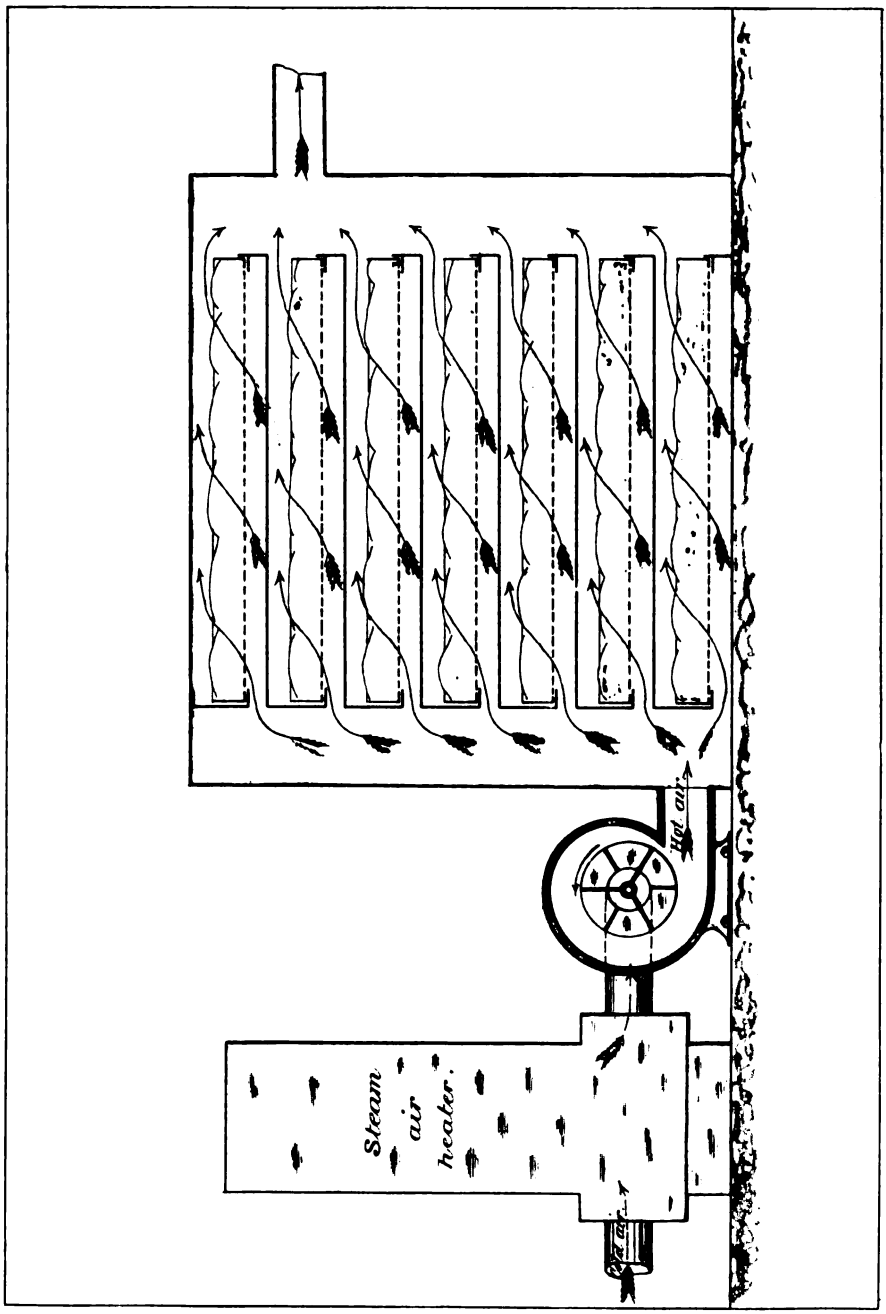

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PLATE 6.

ACID WRINGER.

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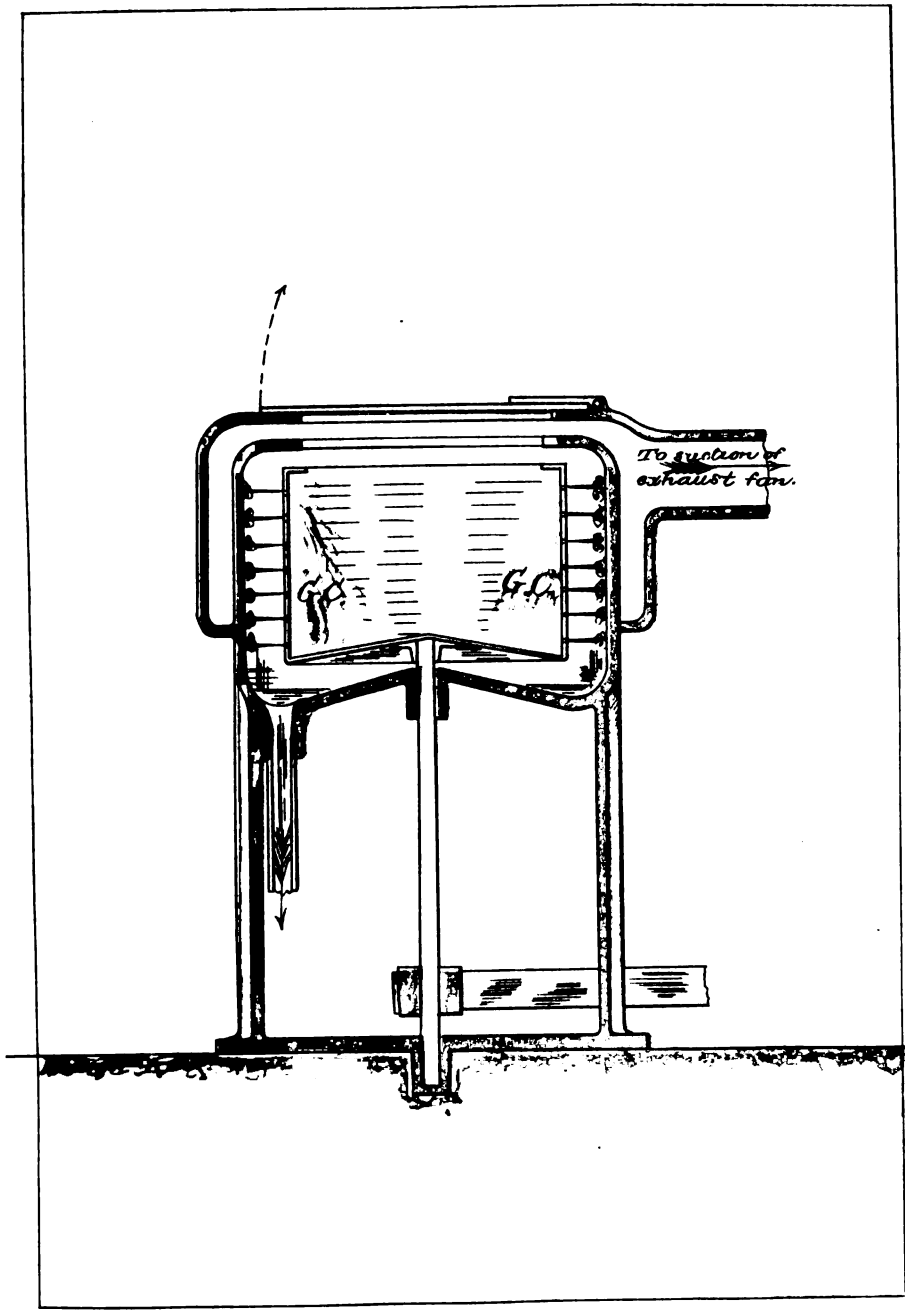

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PLATE 7.

IMMERSION TUB.

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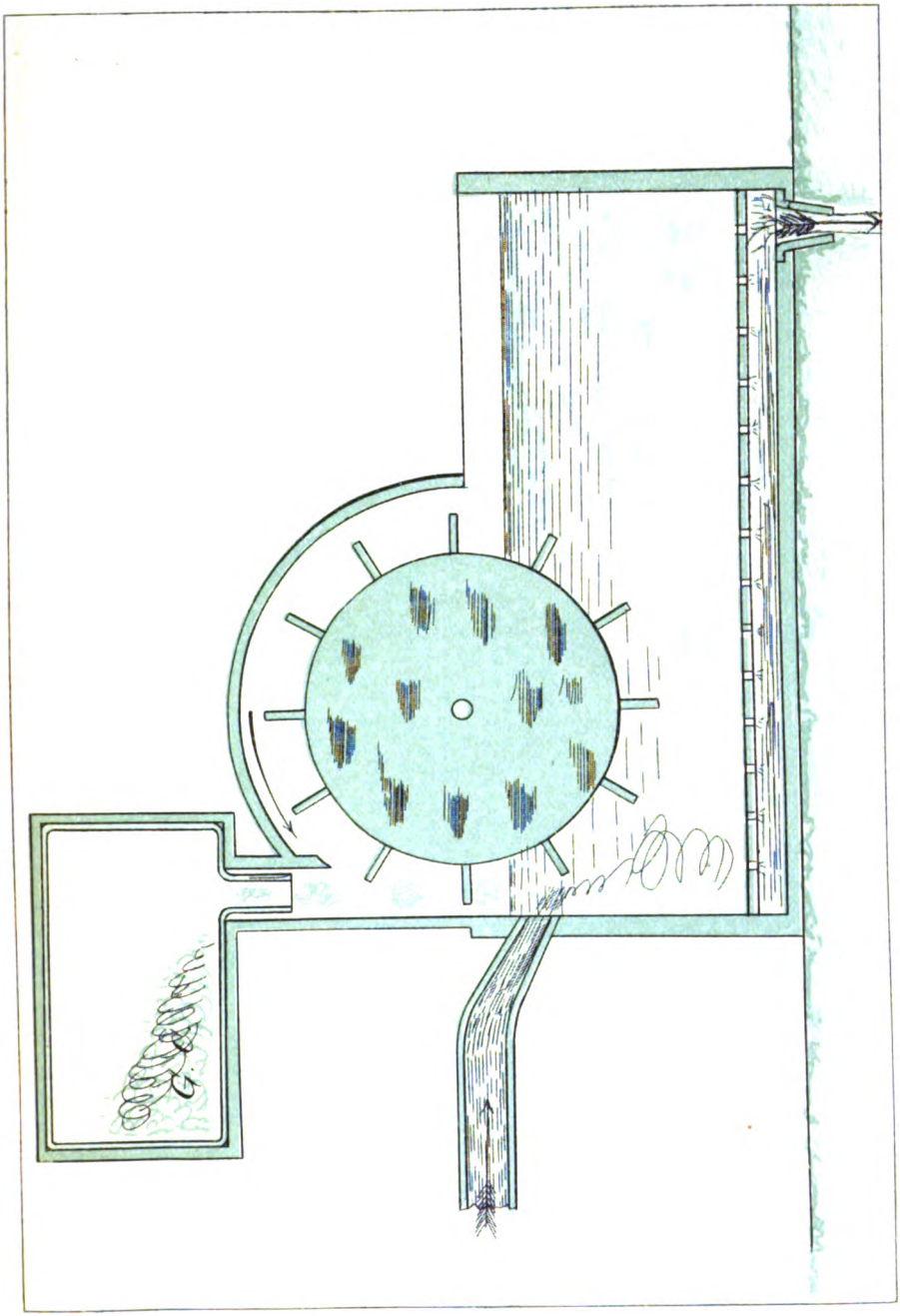

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PLATE 8.

SECOND BOILING TUB.

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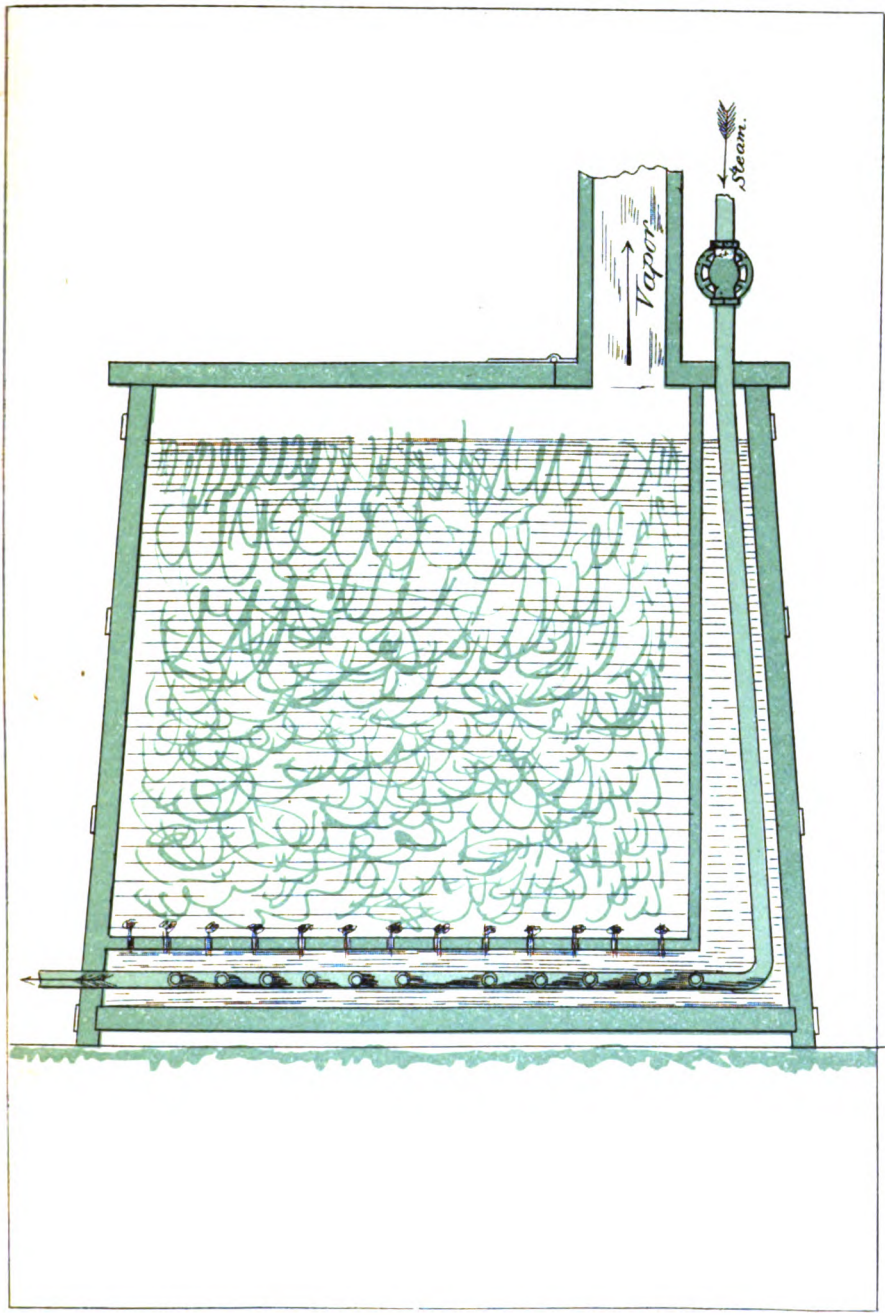

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PLATE 9.

PULPER.

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PLATE 9.

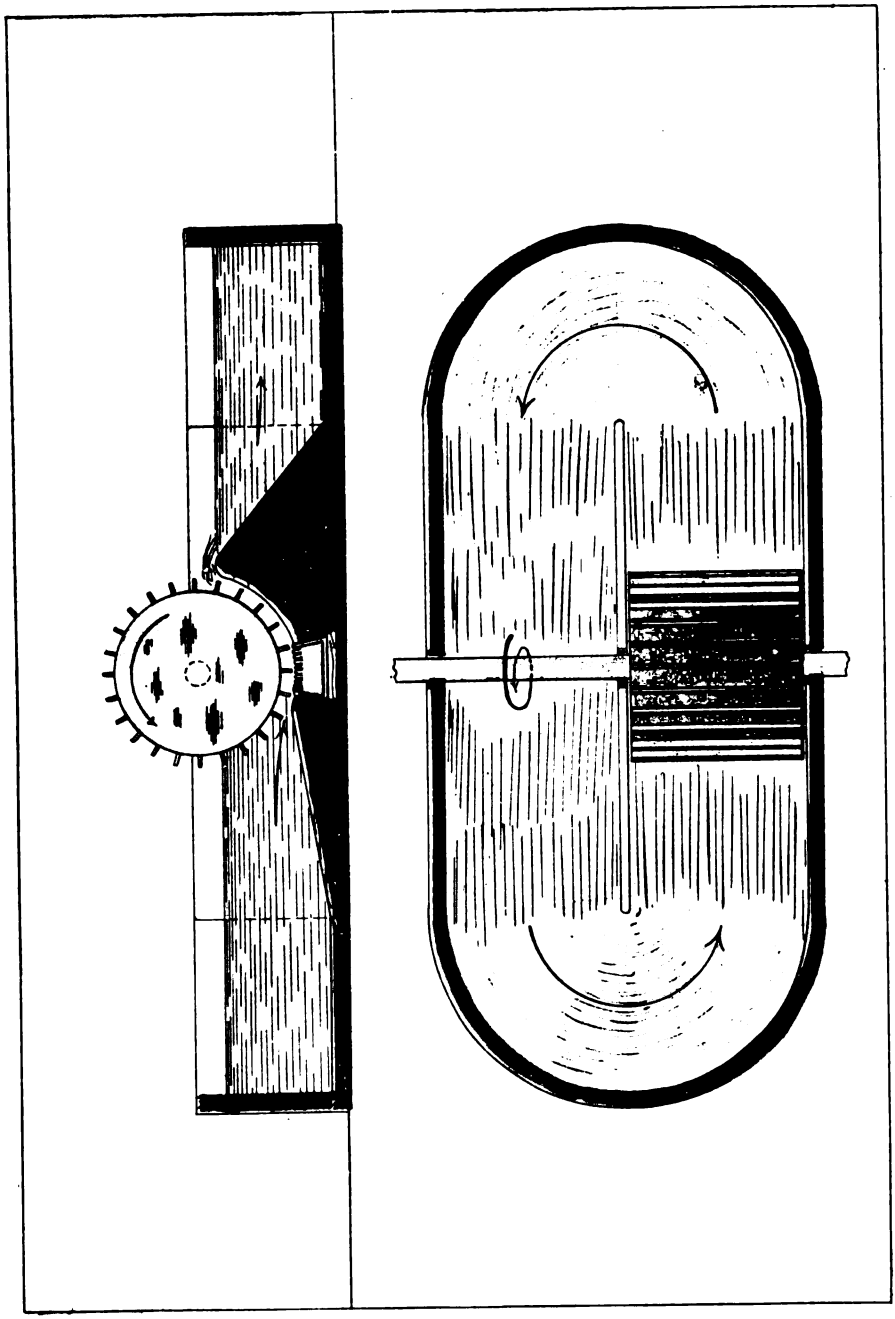

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PLATE 10.

POACHER.

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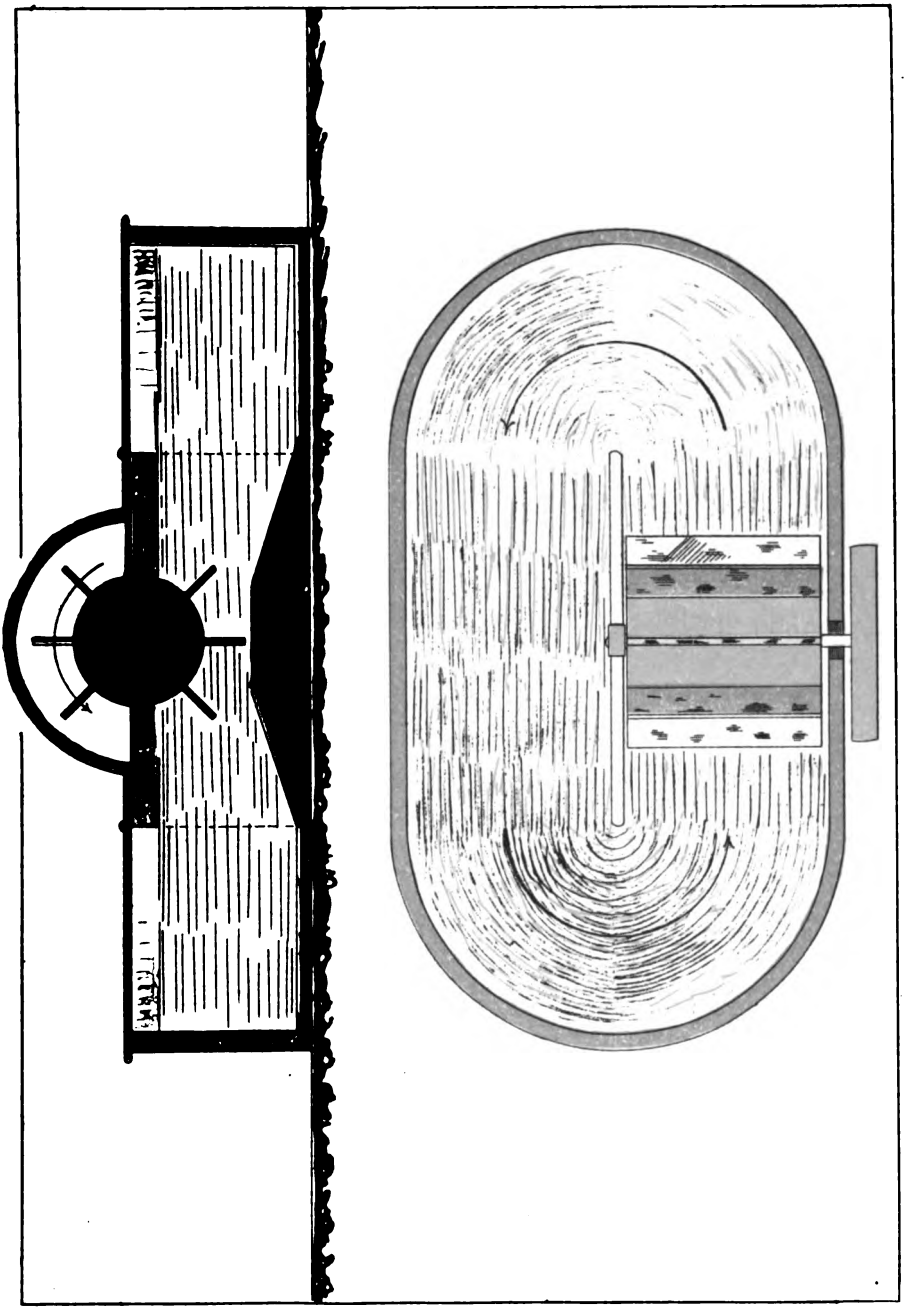

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PLATE 11.

MOLDING PRESS.

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PLATE 11.

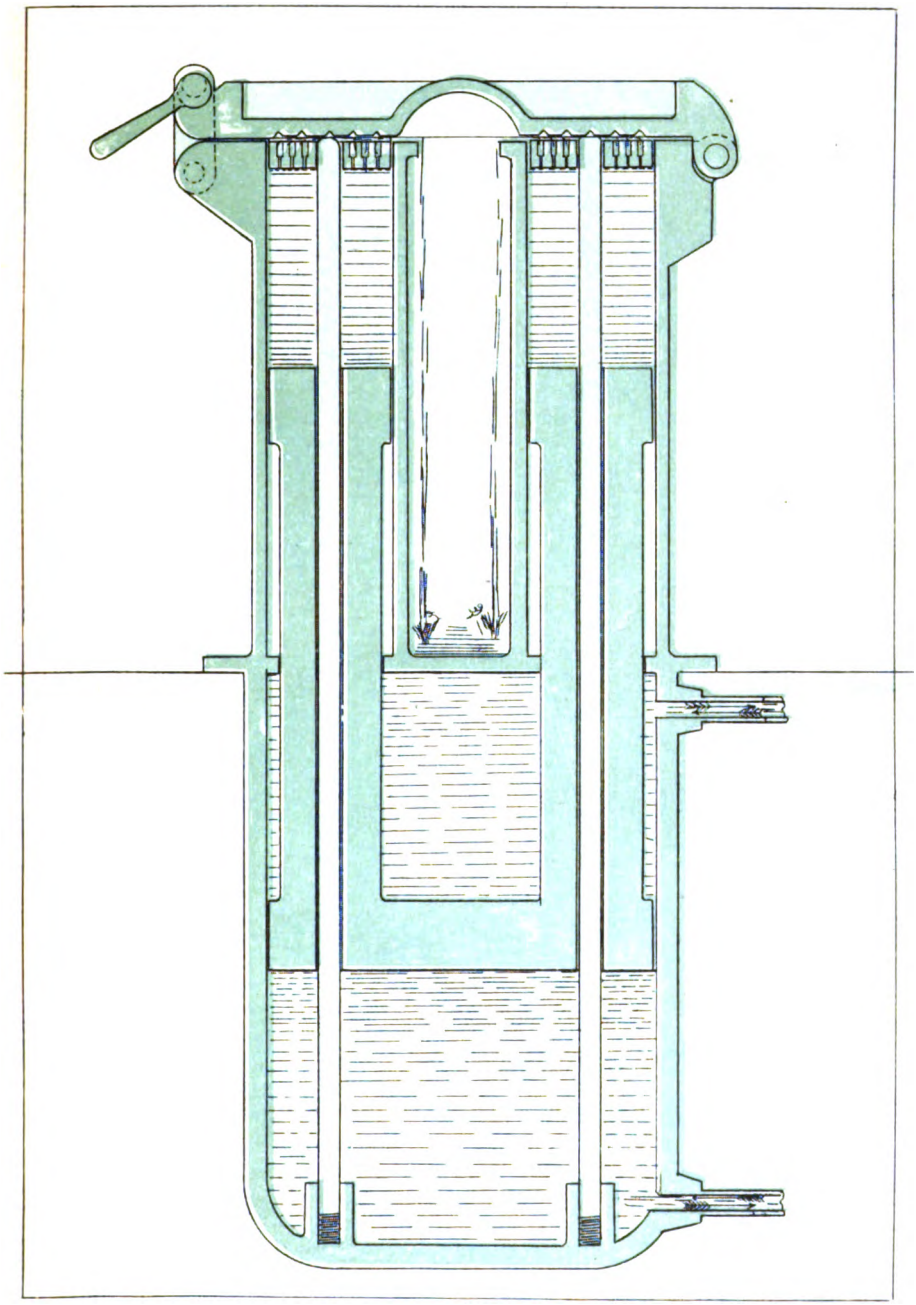

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PLATE 12.

FINAL PRESS.

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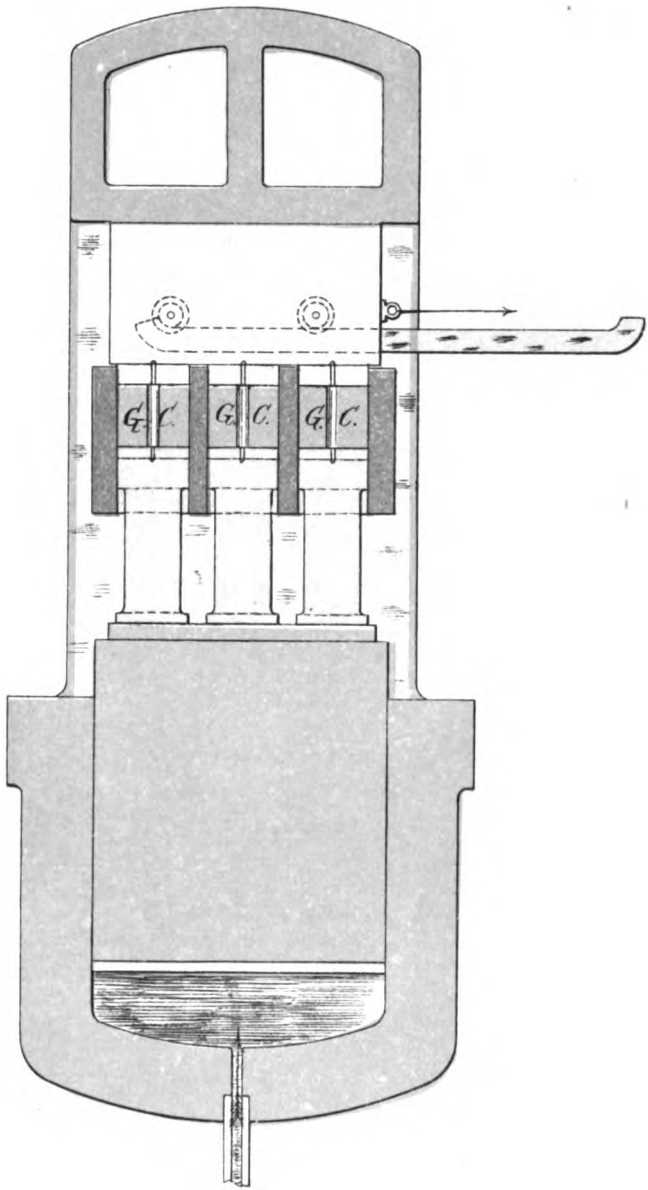
PLATE 12.



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